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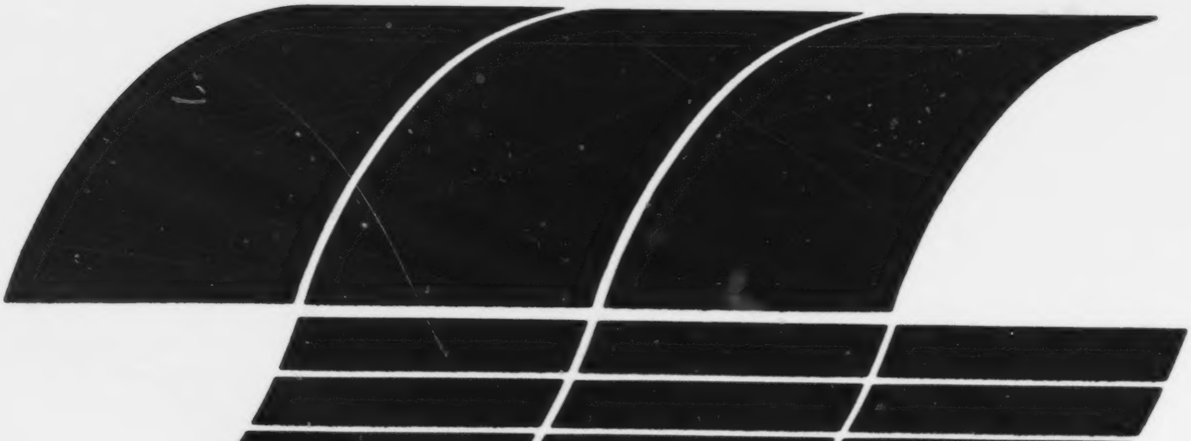
NO_x Abatement for Stationary Sources in Japan

Interagency Energy/Environment R&D Program Report



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16. ABSTRACT The report describes current NOx air pollution problems in Japan and the methods used there to control NOx emissions from stationary sources. The two most common techniques in use are combustion modifications and flue gas treatment (FGT). FGT technologies have been developed more extensively in Japan than in any other country as a result of Japan's stringent NOx emission standards. The various NOx control technologies are examined with respect to both principles of operation and specific process applications. Currently the most popular (over 60 commercial applications) FGT technology is selective catalytic reduction. This technology is capable of 80-90% NOx control and has the lowest cost per kilogram of NOx removed. Recently catalysts have been developed that are resistant to particulate plugging and appear to be applicable to coal-fired boilers in the U.S. Cost and commercial performance data, based on Japanese installations, are presented in much greater detail than was previously available.

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Nitrogen Oxides	Stationary Sources	07B
Combustion	Japan	21B
Flue Gases	Combustion Modification	
Catalysis	Flue Gas Treatment	07D
Reduction	Catalytic Reduction	07C

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NO_x Abatement for Stationary Sources in Japan

by

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Contract No. 68-02-2161
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INTRODUCTION

This report is third in a series of reports on Japanese NO_x control technology authored by Dr. Jumpei Ando. Previous reports in this series are listed below:

EPA 600/7-77-103b	1977
EPA 600/2-76-013b	1976

Recent efforts for air pollution control in Japan have been concentrated on NO_x abatement since ambient SO_2 concentrations have decreased to a level low enough to meet the standard. Although the stringent ambient NO_2 standard promulgated in 1973--a daily average of 0.02 ppm--was amended in July 1978, the new standard is still much more stringent than that in the United States; it cannot be attained in large cities and industrial regions by combustion modification for numerous NO_x sources and by strict NO_x control of automobile exhausts, namely 0.25 g/km. Extensive flue gas treatment for stationary sources is thus required.

Flue gas treatment (FGT) for NO_x control has not been applied in the United States at the present time. However, increasing concern over NO_x emissions and the rapid development of FGT technology are causing U.S. regulatory agencies to consider application of this technology to both utility and industrial boilers. The California Air Resources Board (CARB) has required existing utility boilers in the South Coast Air Quality Management District to achieve 90 percent NO_x control by 1990. Currently, FGT is the only control technology that can achieve this level of control. Also, FGT is being considered by the U.S. Environmental Protection Agency (EPA) in their development of a New Source Performance Standard (NSPS) for industrial boilers.

Application of FGT technology in Japan has preceded any similar application in the U.S. Among the flue gas treatment processes, selective catalytic reduction of NO_x that uses ammonia and catalyst is the most advanced and has been applied to over 60 commercial plants. Other processes, such as selective noncatalytic reduction and simultaneous SO_x and NO_x removal, have also been developed. Many more flue gas treatment plants are required in order to meet the Japanese ambient standard and also to treat new large NO_x sources which are controlled by stringent local regulations. The expanding use of coal will further increase the necessity for flue gas treatment.

The present report will describe the status of energy supply and NO_x concentrations and regulations, as well as the chemistry, technology and problems of NO_x abatement for stationary sources in Japan.

Descriptions in this report are based primarily on Jumpei Ando's visits to plants that use NO_x abatement technologies, his discussions with the users and developers of each process and data made available by them. An exception is Chapter 2, which is based primarily on Katsuya Nagata's investigations.

SUMMARY

COMBUSTION MODIFICATION, SELECTIVE CATALYTIC AND NONCATALYTIC REDUCTION, AND THEIR COMBINATIONS FOR BOILERS

Among technologies for NO_x abatement, combustion modification (CM) and selective catalytic reduction (SCR) that uses catalyst and ammonia at 300-400°C have progressed most remarkably. Selective noncatalytic reduction (SNR) that uses ammonia at 800-1000°C has also been studied extensively and used commercially.

Table 1 shows practical NO_x reduction for flue gas from boilers burning gas, oil and coal with a relatively low nitrogen content by means of CM, SCR, SNR, and combinations thereof.

NO_x can be reduced about 50 percent by using CM with low oxygen combustion, stage combustion, off-stoichiometric combustion, and a low-NO_x burner. About 60-75 percent abatement can be achieved by adding flue gas recirculation. SCR and SNR should be used when further reduction is necessary.

For SCR, catalysts based on TiO_2 have been predominantly used because of the high reactivity and resistance to SO_x. Different shapes of catalysts and types of reactors as shown in Table 2 have been developed for various gases. A dust rich gas may be treated by parallel flow type catalysts and reactors without dust plugging problem.

With SCR, over 90 percent of the NO_x can be removed when one or more moles of NH_3 are used for each mole of NO_x. In this case the concentration of unreacted NH_3 tends to exceed 10 ppm, causing problems such as air

TABLE 1. PRACTICAL NO_x REDUCTION (NO_x and NH_3, ppm)

Fuel	NO_x	By SCR		By SNR		By SNR + SCR[d]	
		NO_x	NH_3	NO_x	NH_3	NO_x	NH_3
Gas	200[a]	30	10	110	25	80	10
	100[b]	20	5	60	20	40	10
	50[c]	10	5	30	10	20	5
Oil	300[a]	40	10	160	30	120	10
	150[b]	25	5	85	25	55	10
	100[c]	20	5	60	20	40	10
Coal	500[a]	50	10	250	50	180	10
	250[b]	35	10	130	30	90	10
	200[c]	30	10	110	25	80	10

[a] Without combustion modification.

[b] With combustion modification excluding flue gas recirculation.

[c] With combustion modification including flue gas recirculation.

[d] Placing a small amount of parallel flow type catalyst in a duct at 300-400°C.

TABLE 2. SCR CATALYSTS AND REACTORS SUITABLE TO VARIOUS GASES

Gas Type	Fuel (Gas source)	Dust (g/Nm^3)	Catalyst Shape	Reactor Type
Clean	Natural gas Kerosene Naphtha	Below 0.03	Granule, Ring	Fixed bed
Semi-dirty	Heavy oil Coal with hot ESP[b]	0.03-0.3	Granule, Ring Honeycomb, Plate	Moving bed Fixed bed[a]
Dirty[c] (dusty)	Coal	15-25	Granule (in elements) Tube, Plate, Honeycomb	Parallel passage Fixed bed[a]
Very dirty[d]	Glass furnace, cement kiln sintering machine (containing alkaline vapor)		Granule	Moving bed

[a] Parallel flow type

[b] Electrostatic precipitator

[c] Treatment may not be easy

[d] Treatment is difficult

preheater plugging by ammonium bisulfate and accumulation of NH_3 in the scrubber liquor of an FGD plant installed downstream of SCR. The NH_3 leakage can be reduced by increasing the amount of catalyst or by adding an ammonia decomposition catalyst, but this practice raises not only the investment cost but also the running cost because of the increased gas pressure drop through the reactor. Therefore, it is preferable to use a smaller amount of NH_3, about 0.85-0.95 moles, to obtain 80-85 percent removal with a NH_3 leakage of 10 ppm or less.

Use of CM together with SCR may be appropriate in most cases because catalyst, NH_3, and power consumption can be reduced. Flue gas recirculation, however, is fairly costly and may not be used with SCR.

SNR is less costly than SCR but gives a low NO_x removal efficiency with a large amount of leak NH , for example, 20-30 ppm for 45 percent NO_x removal. Moreover, SNR is difficult to apply to many existing boilers due to the limited space for NH_3 injection nozzles in a suitable temperature range.

Application of SCR to existing boilers may also be difficult because many of them may have no space for installation of an SCR reactor or for connection of the reactor to the existing duct as shown in Figure 1, A. Even when the space is available, some boilers may not have the excess fan capacity to compensate for the pressure drop of 50-70 mmH_2O required for 80-90 percent NO_x removal by System A of Figure 1.

Parallel flow type catalyst may be placed in an existing duct as shown in B of Figure 1. The major problem with System B is the high gas velocity. The velocity in a duct is usually about 14 m/sec without a catalyst but increases when a catalyst is installed, resulting in a large pressure drop. Moreover, the catalyst may erode with flue gas from coal with a full dust load. Therefore, the amount of the catalyst may be restricted. By using a small amount of the catalyst, 30-50 percent removal with about 10 ppm of

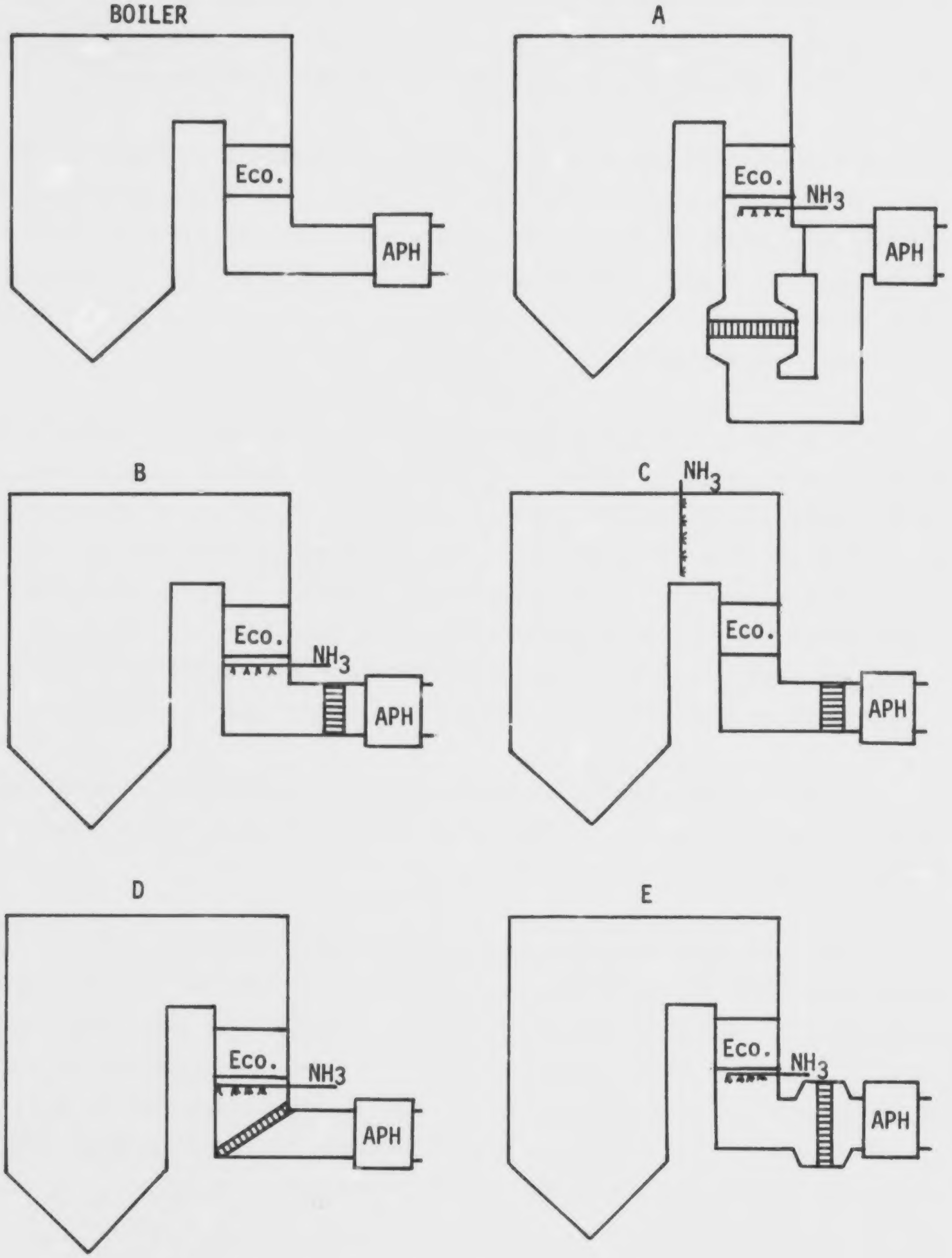
BOILER
Eco.
APH
A
Eco.
NH3
APH
B
Eco.
NH3
APH
C
NH3
Eco.
APH
D
Eco.
NH3
APH
E
Eco.
NH3
APH

Figure 1. Systems for SCR catalyst installation.
(Shaded area indicates catalyst location)

NH_3 leakage may be obtained with a 10-30 H_2O mm pressure drop. If the catalyst is used in combination with SNR as shown in System C of Figure 1, 50-70 percent removal may be attained with 10 ppm of NH_3 leakage.

If the catalyst can be placed as shown in System D of Figure 1, the gas velocity may not be exceedingly high and 60-70 percent removal may be obtained with about 10 ppm of NH_3 leakage and a pressure drop of 30-50 mmH_2O. If there is not enough room for mixing NH_3 with gas, NH_3 may be injected upstream of the economizer. NH_3 may be injected in a hot zone (800-1000°C) for further NO_x abatement.

If a portion of the duct between the economizer and air preheater can be enlarged as shown in System E of Figure 1, any type of catalyst may be used to obtain 80-90 percent removal with less than 10 ppm of NH_3 leakage and a pressure drop of 40-60 mmH_2O. The depth of the catalyst bed (the length in the direction of gas flow) may be about 2 m with a honeycomb catalyst and longer with parallel-passage and parallel-plate catalysts. A larger diameter of the reactor may be needed when a granular catalyst is used because the catalyst bed requires a smaller gas velocity.

System E is less costly than System A and suitable for a new boiler. When an additional fan is needed for an existing boiler, System A may be suitable because it has space for the fan.

There have been arguments about the necessity for CM when SCR is installed. Flue gas recirculation is costly. It requires extensive duct work and a fan and therefore may not be used when SCR is installed. Other measures for CM which are less costly may be used in combination with SCR or SNR because CM reduces the catalyst and ammonia requirement to some extent. Decisions on the use of the CM methods should be based on cost comparison and the allowable NO_x and NH_3 emissions.

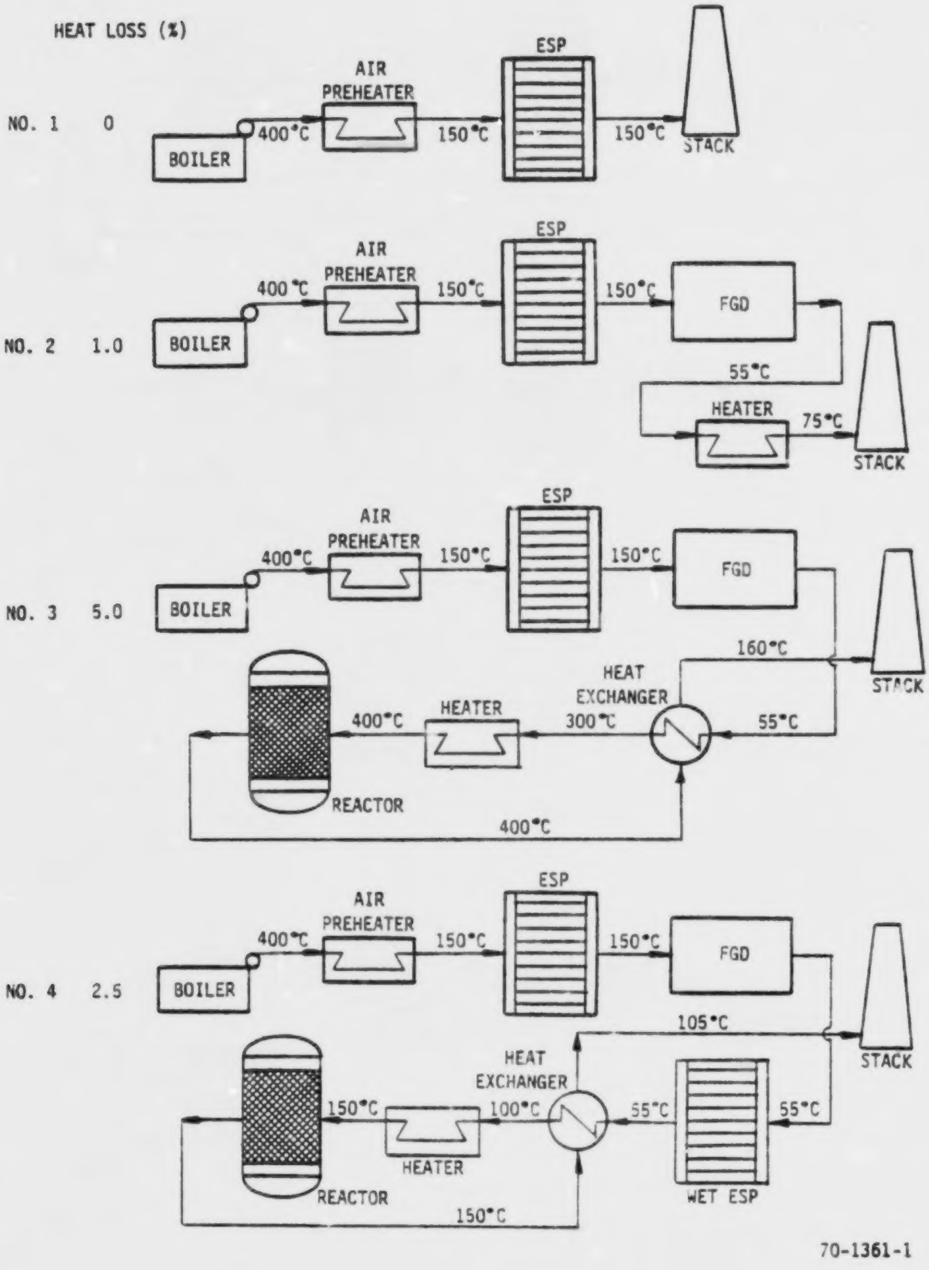
HEAT LOSS (%)
NO. 1
0
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
STACK
NO. 2
1.0
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
FGD
55°C
HEATER
75°C
STACK
NO. 3
5.0
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
FGD
160°C
STACK
HEAT EXCHANGER
400°C
HEATER
300°C
55°C
REACTOR
400°C
NO. 4
2.5
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
FGD
105°C
STACK
HEAT EXCHANGER
150°C
100°C
55°C
55°C
HEATER
REACTOR
WET ESP
150°C
70-1361-1

Figure 2. Combined and simultaneous removal systems (figures show temperatures, °C).

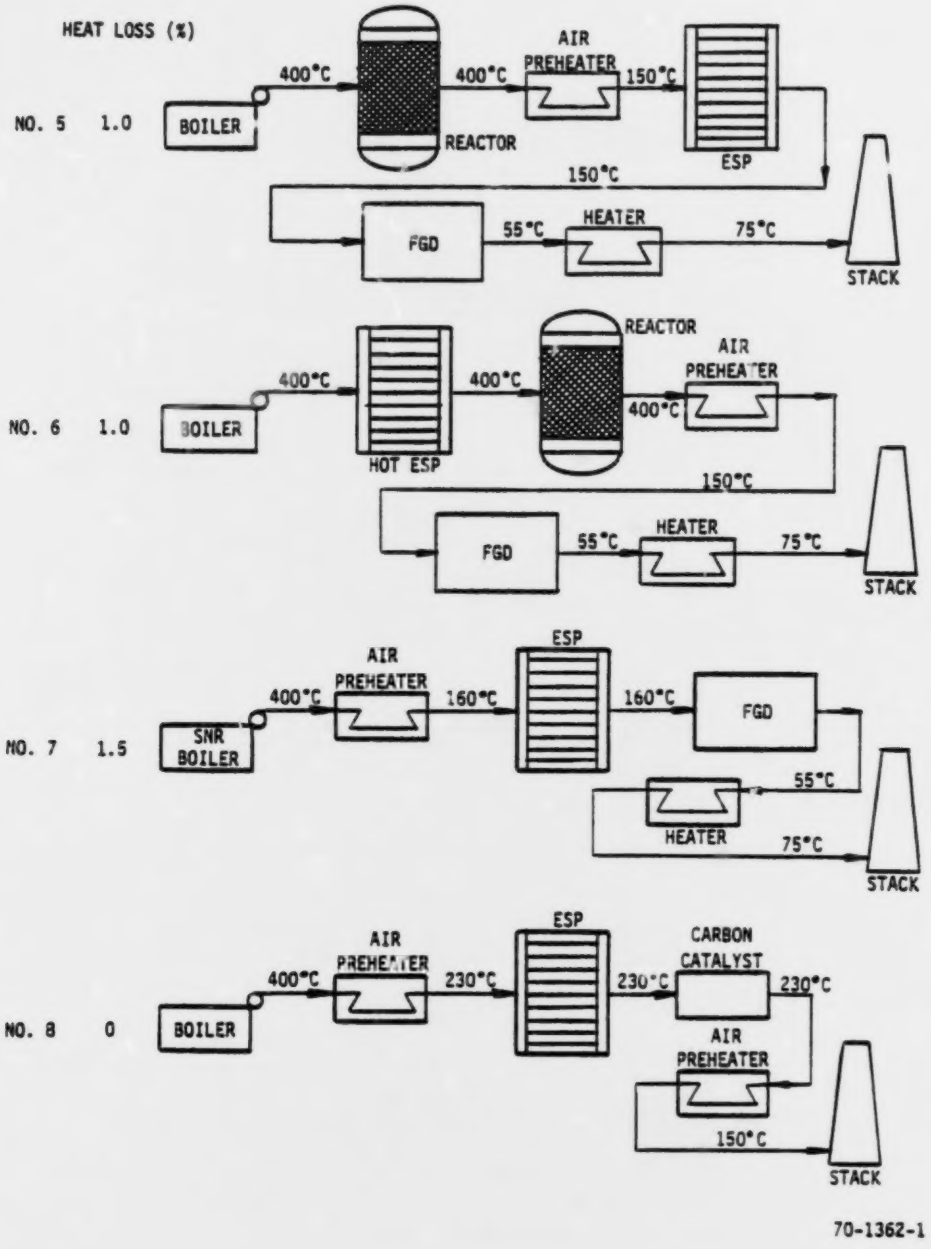
HEAT LOSS (%)
NO. 5
1.0
BOILER
400°C
REACTOR
400°C
AIR PREHEATER
150°C
ESP
150°C
FGD
55°C
HEATER
75°C
STACK
NO. 6
1.0
BOILER
400°C
HOT ESP
400°C
REACTOR
400°C
AIR PREHEATER
150°C
FGD
55°C
HEATER
75°C
STACK
NO. 7
1.5
SNR BOILER
400°C
AIR PREHEATER
160°C
ESP
160°C
FGD
55°C
HEATER
75°C
STACK
NO. 8
0
BOILER
400°C
AIR PREHEATER
230°C
ESP
230°C
CARBON CATALYST
230°C
AIR PREHEATER
150°C
STACK
70-1362-1

Figure 2. Continued.

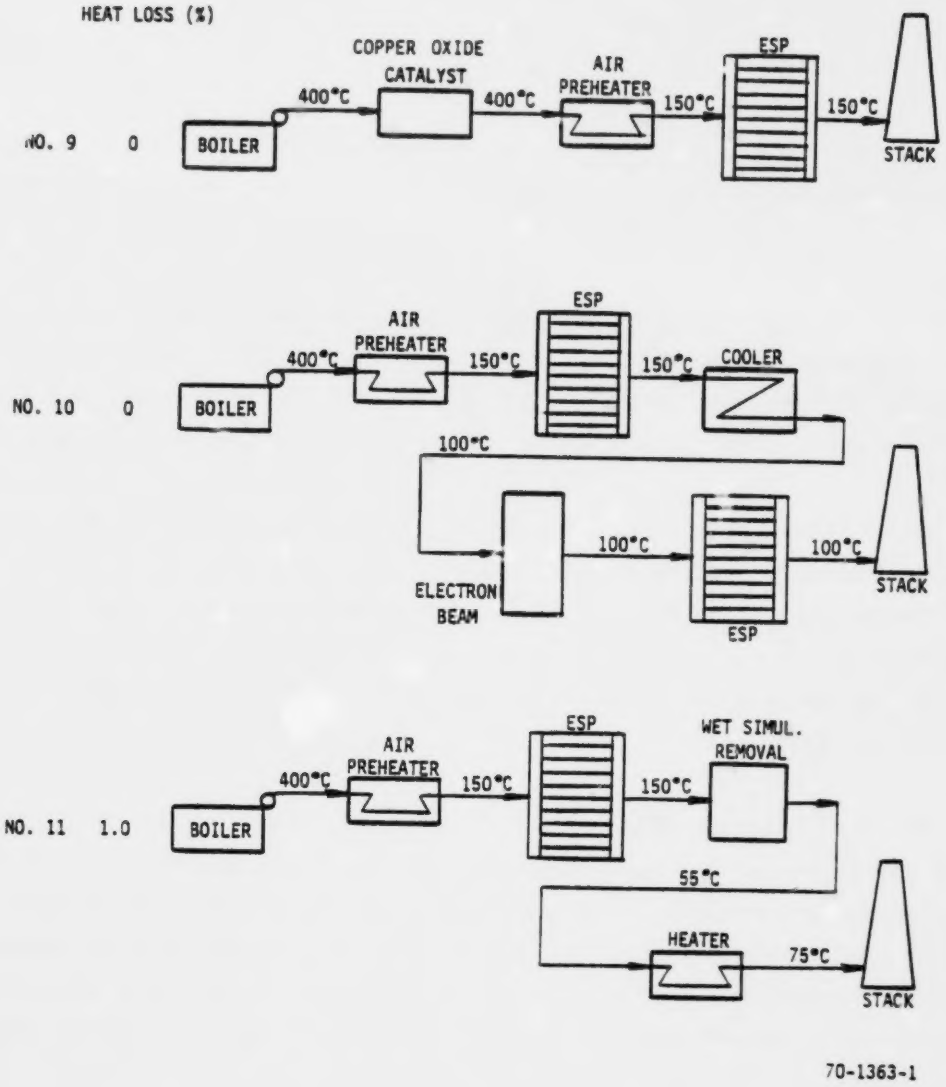
HEAT LOSS (%)
NO. 9
0
BOILER
400°C
COPPER OXIDE CATALYST
400°C
AIR PREHEATER
150°C
ESP
150°C
STACK
NO. 10
0
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
COOLER
100°C
ELECTRON BEAM
100°C
ESP
100°C
STACK
NO. 11
1.0
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
WET SIMUL. REMOVAL
55°C
HEATER
75°C
STACK
70-1363-1

Figure 2. Continued.

A combination of CM, SNR and SCR may be useful when Systems A and E shown in Figure 1 cannot be used and the combination of CM and the Systems B or D is not sufficient.

NO_x and SO_x REMOVAL

Figure 2 shows schematically the temperature and heat loss of various systems, FGD, combination of FGD and SCR, simultaneous removal processes, etc.

No. 1 of Figure 2 shows gas temperatures at regular boiler operation, which is considered standard (no heat loss). No. 2 illustrates the application of FGD with gas reheating from 55 to 75°C, which accounts for a heat loss of about 1 percent (equivalent to about 1 percent of boiler input).

No. 3 shows the application of FGD to clean the gas before SCR. The combination causes much heat loss (about 5 percent), and yet is not free from the ammonium bisulfate problem because FGD, although it removes over 90 percent of the SO_2, does not remove SO_3 sufficiently. Moreover, mist from FGD aggravates the problems of deposits in the heat exchanger and on the SCR catalyst.

No. 4 is a modification of No. 3 with a wet electrostatic precipitator after FGD (ahead of the heat exchanger) to remove SO_3 and mists and a low temperature catalyst to reduce heat loss. The low temperature catalyst, however, may not be resistant to SO_x and with its use SO_x must be reduced to 1 ppm (Section 4.9). Usually, sodium hydroxide scrubbing is needed in addition to a conventional FGD system. Although the gas is cleaned well by such treatments, the system may be fairly costly.

No. 5 is considered a most practical system for NO_x and SO_x control. The gas at 350-400°C from a boiler economizer is treated by SCR and then by FGD. SO_x-resistant catalysts and reactors virtually free from particulate plugging have been developed and are now commercially available. Parallel flow type reactors may be able to treat even a flue gas from a coal-fired boiler with full particulate load. The ammonium bisulfate problem with the air preheater may not be serious for flue gas from low-sulfur fuels which contain little SO_x and also for flue gas from coal whose fly ash has a sweeping effect, provided that NH_3 at the SCR reactor outlet is kept at a low concentration, preferably below 5 ppm. The bisulfate may cause some problem with a flue gas from a high-sulfur oil.

The bisulfate deposits on the SCR catalyst treating SO_x-rich flue gas when the gas temperature drops below about 320°C due to the reduction of boiler load. The deposit may not be a problem if the low-temperature period is limited to a few hours a day, because the bisulfate is removed when the gas temperature is raised above 350°C. For some of the boilers, however, a device to maintain the temperature above about 320°C, such as a by-pass system of a hot gas or an auxiliary burner, may be needed.

Another problem for the No. 5 system is the accumulation of ammonia in the scrubber (or prescrubber) liquor of the FGD system. This may not be a problem for FGD with ammonia scrubbing. For other FGD processes, it may be necessary to remove the ammonia from the scrubber liquor, as has been done at the Owase plant, Chubu Electric.[1] The Owase plant has no SCR system but injects a small amount of NH_3 between an air preheater and electrostatic precipitator to prevent precipitator corrosion by SO_3. Since a portion of the NH_3 goes into a lime-gypsum FGD system and is caught by a prescrubber, lime addition has been used to strip ammonia from the prescrubber liquor.

The No. 6 system involves the use of a hot electrostatic precipitator. It may be suitable for a flue gas from a low-sulfur coal whose fly ash is not caught efficiently by a cold electrostatic precipitator. Either the parallel flow type or the moving bed type SCR reactor can be used because the ash content of the gas may be reduced to about 200 mg/Nm^3 by the precipitator. The ammonium bisulfate deposit problem in the air preheater may be more serious with system No. 6 than with system No. 5 because the gas of No. 6 contains less fly ash for the sweeping effect for removing ammonium bisulfite. The problems of the bisulfate deposit on the catalyst and ammonia accumulation in the scrubber liquor are the same as with system No. 5.

No. 7 is a combination of SNR (selective noncatalytic reduction) and FGD. Since the NH_3 concentration at the boiler outlet is much higher than at the SCR reactor outlet, the problems of ammonium bisulfate deposit in the air preheater and ammonia accumulation in the FGD scrubber are more serious than with systems 5 and 6. NH_3 must be removed from scrubbing liquor to eliminate NH_3 in wastewater. Consequent heat loss might be slightly higher than with No. 5 and No. 6. It may be preferable to use a small amount of SCR catalyst to reduce the NH_3 leakage and to increase the NO_x removal efficiency, particularly when the process is used with an FGD system other than ammonia scrubbing.

Systems Nos. 8-10 show dry simultaneous removal processes which are expected to involve no heat loss, although a considerable amount of energy is required for plant operation. Both the carbon and the CuO processes have been considered costly for FGD, but the capability of simultaneous removal may compensate for the disadvantage. The electron beam process has been tested in a small pilot plant; larger-scale tests are needed to evaluate its commercial feasibility.

System No. 11 shows a wet simultaneous removal process with the same level of heat loss as FGD. The process problems are described in Chapter 7; further improvement is required for commercial application.

SUITABLE PROCESSES FOR VARIOUS SO_x AND NO_x CONCENTRATIONS

The relationships of SO_x and NO_x concentrations in gas to suitable treatment processes are illustrated in Figure 3. The combination of SCR followed by FGD can be used for all gas compositions, but there may be an ammonium bisulfate problem for a gas rich in SO_x. SNR should be used for a gas with a relatively low NO_x concentration for which about 45 percent NO_x removal is sufficient and with a low SO_x concentration which does not require FGD, because the NH_3 leakage may be a considerable problem to FGD.

Dry simultaneous removal processes suit gases with a relatively small SO_x/NO_x ratio for the following reasons:

1) For the carbon process, carbon consumption increases with SO_x concentration.

2) For the metal oxide processes such as the Shell process, a high SO_x concentration increases hydrogen and steam consumption and also tends to lower NO_x removal efficiency (see Section 6.5.2).

3) For the electron beam process, the by-product is a lower quality fertilizer when the gas is rich in SO_x.

Use of the carbon and electron beam processes may be restricted to gases containing less than about 400 ppm SO_x. For the Shell process, about 70 percent NO_x removal may be a practical limit unless the amount of catalyst (acceptor) is increased considerably.

On the other hand, wet simultaneous removal processes suit a gas rich in SO_2 and relatively low in NO_x because an SO_2/NO_x mole ratio of 4-5 is usually required to achieve over 80 percent NO_x removal. Moreover, equipment for conversion of FGD units to accommodate NO_x removal is smaller and less costly with a low NO_x concentration. Application of the oxidation-absorption-reduction process may be limited to gases containing less than about 150 ppm of NO because of the cost of the oxidizing agent. Absorption-reduction processes may be used for gases with relatively high NO_x concentrations. Although 90 percent NO_x removal can be achieved by the wet processes, 70-80 percent removal may be more practical. Ninety percent removal requires a large L/G ratio or an excessive amount of oxidizing agent, which tends to form a hard-to-treat nitrate wastewater.

COSTS OF NO_x AND SO_x REMOVAL

Figures 4 and 5 show investment costs in battery limits of NO_x and SO_x removal plants with capacities of up to 1,000,000 Nm^3/hr of flue gas from a boiler, equivalent to 330 MW with oil and 280 MW with coal. Figure 6 shows annualized operating costs for 8000 hours of yearly operation including 7 years of depreciation. It is assumed that total investment costs are 50 percent more than the investment costs in battery limits. The costs are based on the investigations by Environment Agency[2] with modifications by Ando based on his study and represent low costs which may be attained. The costs per kW or kWhr for flue gas from coal may be about 20 percent more than those for flue gas from oil because of the larger gas volume per kW.

The costs for SCR by the direct process, that is, treating directly the flue gas from a boiler economizer, are 3000-4000 yen/kW ($15-20/kW) investment costs and 0.3-0.4 yen/kWhr ($0.00015-0.00020/kWhr) operating cost with a 200-300 MW size plant for flue gas from an oil-fired boiler, and are about one-fourth those for FGD.

The costs for SCR with gas heating by a heat exchanger and a heater are about double those for direct SCR and are about half those for FGD.

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Use of the carbon and electron beam processes may be restricted to gases containing less than about 400 ppm SO_x. For the Shell process, about 70 percent NO_x removal may be a practical limit unless the amount of catalyst (acceptor) is increased considerably.

On the other hand, wet simultaneous removal processes suit a gas rich in SO_2 and relatively low in NO_x because an SO_2/NO_x mole ratio of 4-5 is usually required to achieve over 80 percent NO_x removal. Moreover, equipment for conversion of FGD units to accommodate NO_x removal is smaller and

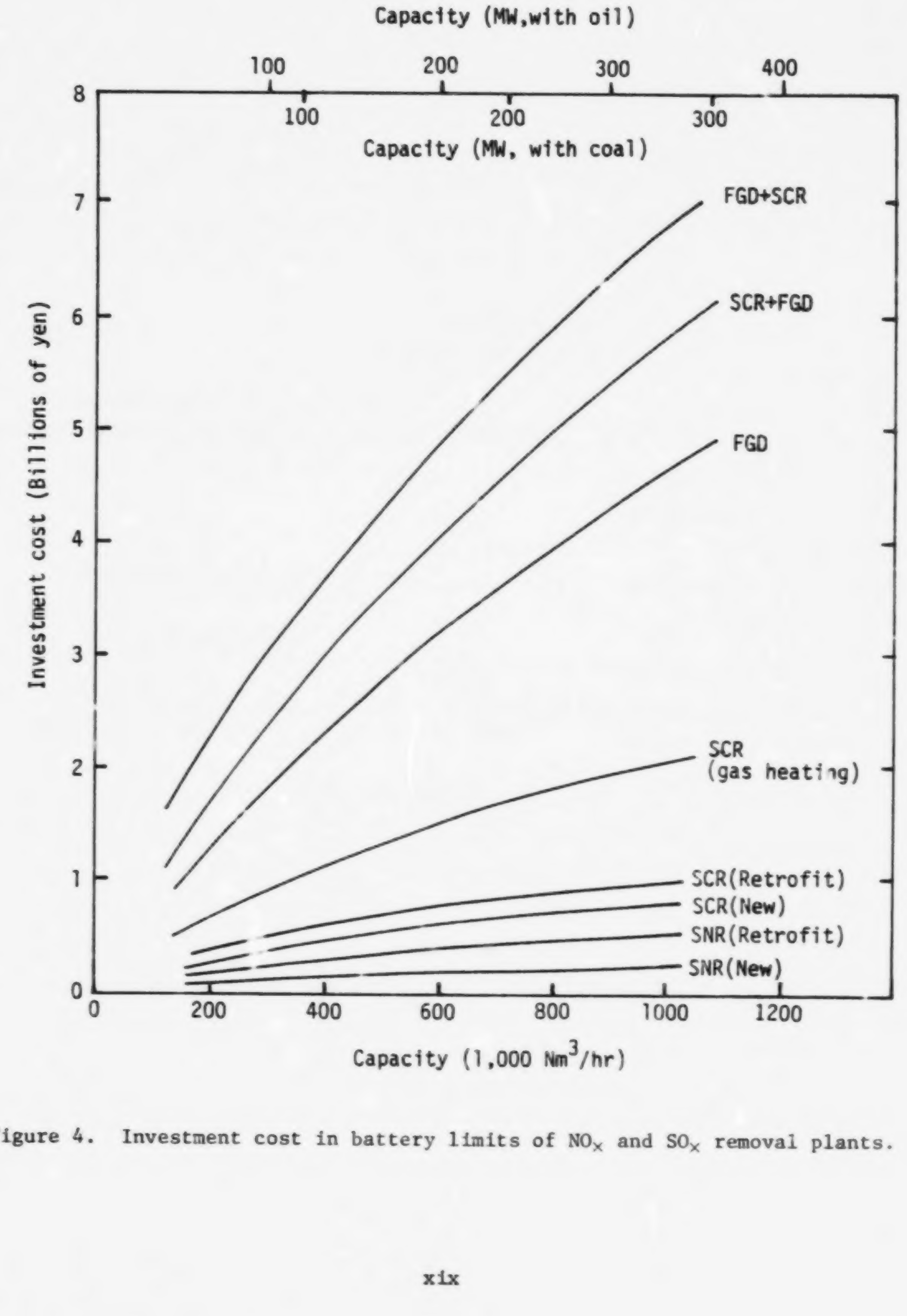

Figure 4. Investment cost in battery limits of NO_x and SO_x removal plants.

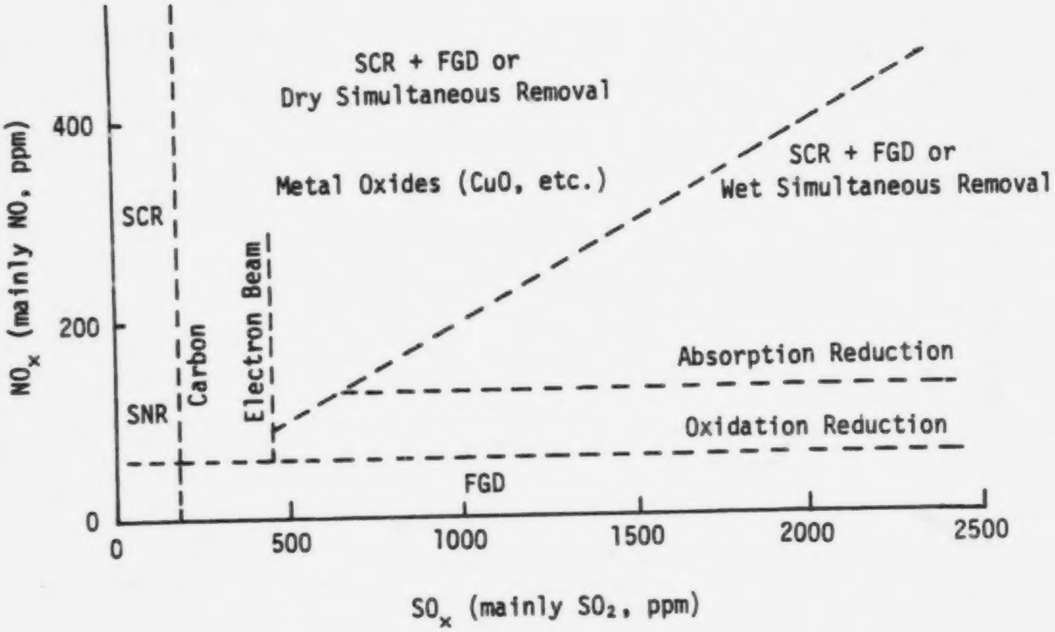

Figure 3. Suitable processes for various gas compositions.

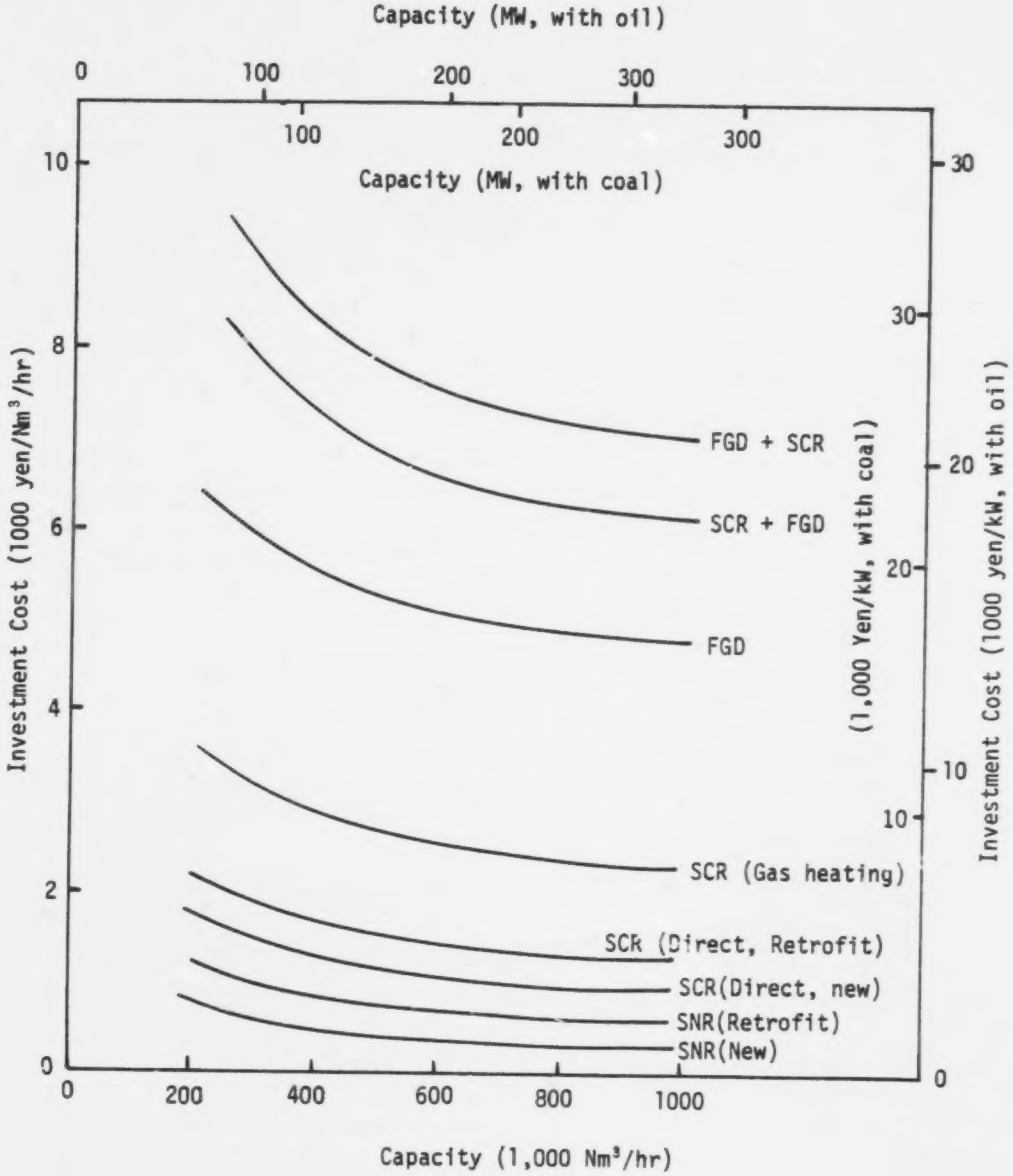

Figure 5. Investment cost in battery limits per unit capacity of NO_x and SO_x removal plants

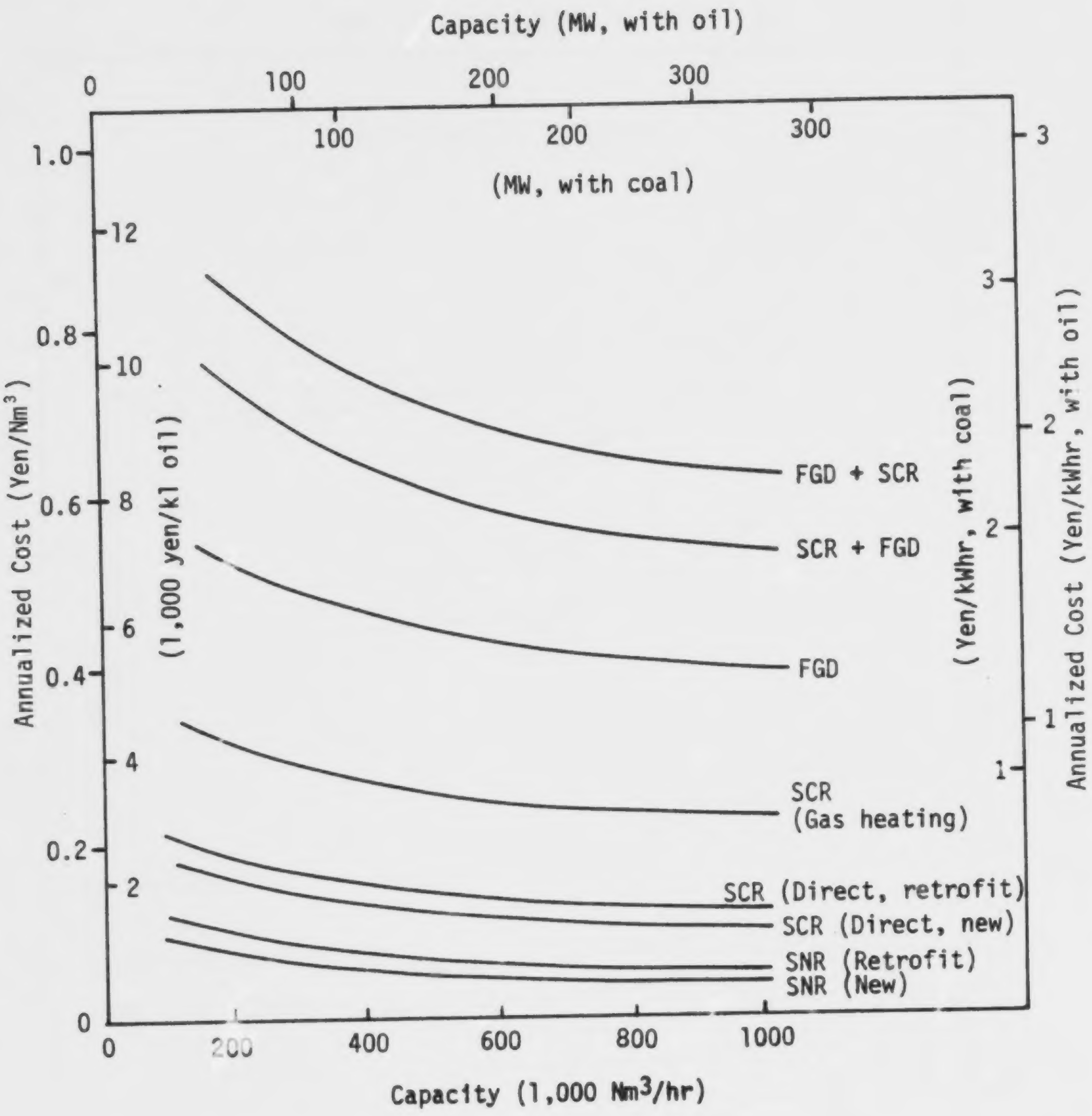

Figure 6. Annualized operation costs for NO_x and SO_x removal plants.

The costs for SNR are half to one-third those for direct SCR, but NO_x removal efficiency is about half that of SCR (40-45 percent versus 80-90 percent). The problems with SNR due to the larger amount of ammonia leakage might add some actual operation cost.

The combination of SCR followed by FGD, as shown in No. 5 of Figure 2, costs a little more than the sum of the costs for direct SCR and FGD because removal of the ammonia from the FGD scrubber liquor is required. The costs, however, are still considerably lower than those for the combination of FGD followed by SCR, which requires gas reheating as shown in No. 3 of Figure 2.

The costs for the dry and wet simultaneous removal processes are as yet uncertain but seem to be close to those for the combination of FGD followed by SCR.

CONCLUSIONS

There has been considerable progress with combustion modification. It currently can reduce NO_x in flue gases from utility boilers to 50 ppm for gas burning, 100 ppm for oil burning, and 200 ppm for coal burning.

There have also been considerable advances with selective catalytic reduction (SCR) to the extent that SO_x-resistant catalysts and reactors free from particulate plugging have been commercialized. By using the direct process to treat directly the flue gas from a boiler economizer, the SCR cost has been reduced to about one-fourth the FGD cost. Operation of SCR is easy and can be controlled from a boiler control room by one of the boiler operators. The ammonium bisulfate problem has been nearly solved for flue gases from coal and low-sulfur oil, although further studies are needed particularly for flue gas from a high-sulfur oil.

As a result of these advances, many large SCR plants have been constructed mainly for boilers which burn gas and low-sulfur oil. A demonstration plant for an existing coal-fired boiler (about 250 MW) will be constructed in the near future. Although SCR can achieve over 90 percent NO_x removal without difficulty, it may be appropriate to reduce the amount of ammonia and obtain 80-85 percent removal with ammonia leakage kept at less than about 5 ppm. The pressure drop of the gas in the reactor may be kept at 40-60 mmH_2O.

Selective noncatalytic reduction (SNR) may be useful for an existing boiler for which 40-50 percent NO_x removal is sufficient and which has no room for installation of an SCR reactor or no excessive fan capacity to compensate for the pressure drop caused by the reactor. Since there is a considerable amount of ammonia leakage with SNR, it may be desirable to place a small amount of SCR catalyst (parallel flow type) in a duct at 350-400°C to reduce the ammonia leakage and to increase the NO_x removal efficiency. With this combination, an NO_x removal efficiency of 60-70 percent with 10 ppm of leak NH_3 may be attained with a pressure drop of 15-30 mmH_2O.

The commercial applicability of the simultaneous removal processes, dry and wet, to remove over 80 percent of the NO_x and SO_2 has not been confirmed yet because the processes are still undergoing pilot plant tests. There should be no heat loss with the dry simultaneous removal processes, as shown in Nos. 8-10 of Figure 2. These processes, however, require considerable energy for plant operation and production of reducing agents.

Since all of these dry NO_x removal and simultaneous removal processes require ammonia, it is possible that the world supply of ammonia will run short when these processes are applied extensively in many countries. On the other hand, wet simultaneous removal processes can convert NO_x to NH_3. Although there are problems with the wet simultaneous processes as already mentioned, further studies may solve the problems.

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CONVERSION FACTORS AND ABBREVIATIONS

CONVERSION FACTORS

The metric system is used in this report. Following are some factors for conversion between metric and English systems:

1 m (meter) = 3.3 feet
1 m^3 (cubic meter) = 35.3 cubic feet
1 t (metric ton) = 1.1 short tons
1 kg (kilogram) = 2.2 pounds
1 liter = 0.26 gallon
1 kl (kiloliter) = 6.19 barrels

Gas flow rates are expressed in Nm^3/hr (normal cubic meters per hour).

1 Nm^3/hr = 0.59 standard cubic foot per minute

L/G ratio (liquid/gas ratio) is expressed in liters/Nm^3.

1 liter/Nm^3 = 7.4 gallons/thousand standard cubic feet

YEN-DOLLAR CONVERSION

Wherever possible in the report where costs in yen are presented, the equivalent cost in U.S. dollars is also presented. The exchange rate used to make these conversions was 200 yen/$ and this figure should be used when converting cost data presented in graphs since the graphical data is presented in terms of yen.

ABBREVIATIONS

FGT = Flue gas treatment
FGD = Flue gas desulfurization
CM = Combustion modification
SV = Space velocity
SCR = Selective catalytic reduction
SNR = Selective noncatalytic reduction
ESP = Electrostatic precipitator
kW = Kilowatt
kWh = Kilowatt hour
MW = Megawatt
LNG = Liquified natural gas
L/G = Liquid-to-gas ratio
Nm^3/hr = Normal cubic meters per hour (0°C, 101,325 Pa)

SECTION 1

NO_x CONCENTRATION, REGULATION AND ABATEMENT IN JAPAN

1.1 INTRODUCTION

In Japan, ambient SO_2 concentrations have decreased remarkably due to the use of low-sulfur fuels and flue gas desulfurization. As a result, recent efforts for air pollution control have been concentrated on the reduction of NO_x (Figures 1-1 and 1-2).

Man-made emissions of NO_x in Japan have totaled nearly 2 million tons yearly. About 65 percent are derived from stationary sources, while in large cities 60 to 70 percent are attributed to mobile sources. Yearly average NO_2 concentrations in major Japanese cities are compared with those in several major world cities in Figure 1-3. This figure shows that NO_2 concentrations in the Japanese cities do not exceed the U.S. air quality (ambient) standard, but are much higher than the 1973 Japanese standard. The U.S. standard is a yearly average of 0.05 ppm, while the 1973 Japanese standard is a yearly average of about 0.01 ppm (a daily average of 0.02 ppm)--the most stringent in the world.

The 1973 standard was based principally on animal tests, which gave results similar to those obtained in the United States. The large difference in the standards of the two countries is due to the difference in the safety factors. Since compliance to the Japanese standard is voluntary, a large safety factor was used for NO_2 to ensure public health and to prevent photochemical smog. Conformance to this standard was to be attained within 5 years in most districts and within 8 years in polluted cities such as Tokyo and Osaka, which have a daily average of 0.06-0.08 ppm NO_2. For the

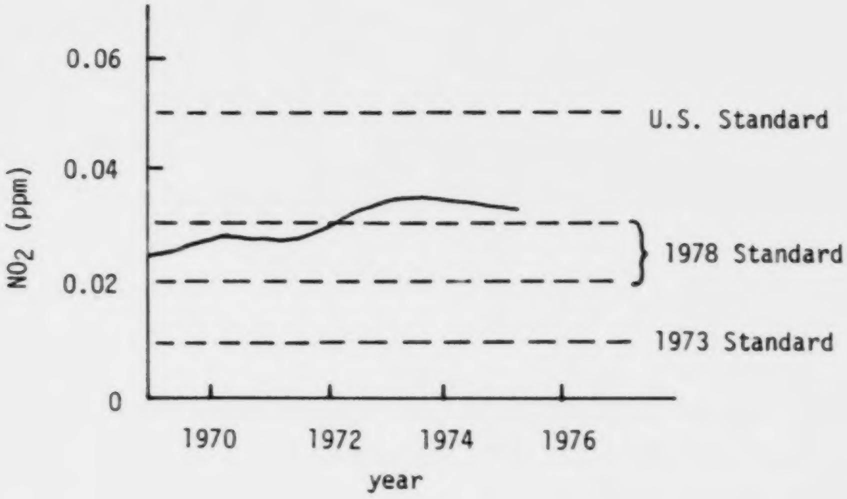

Figure 1-1. Comparison of U.S. and Japanese ambient NO_2 standards and yearly average concentrations of 6 Japanese stations.

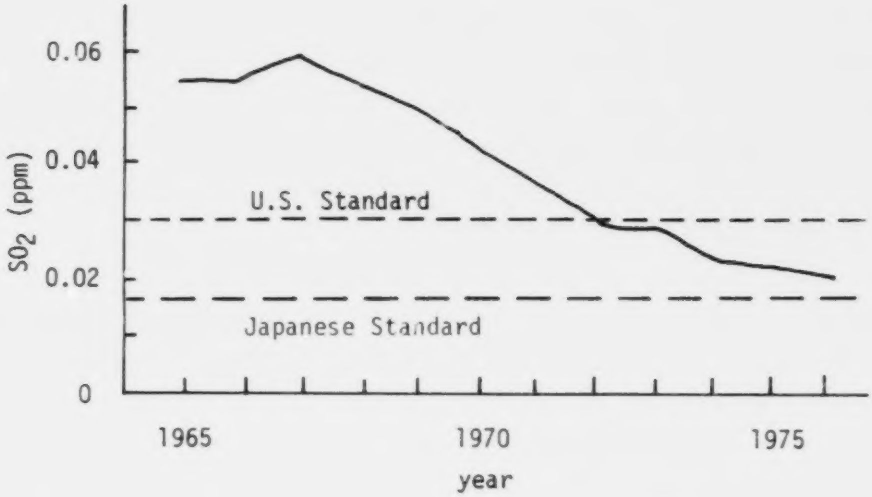

Figure 1-2. Comparison of U.S. and Japanese ambient SO_2 standards and yearly average concentrations of 15 Japanese stations.

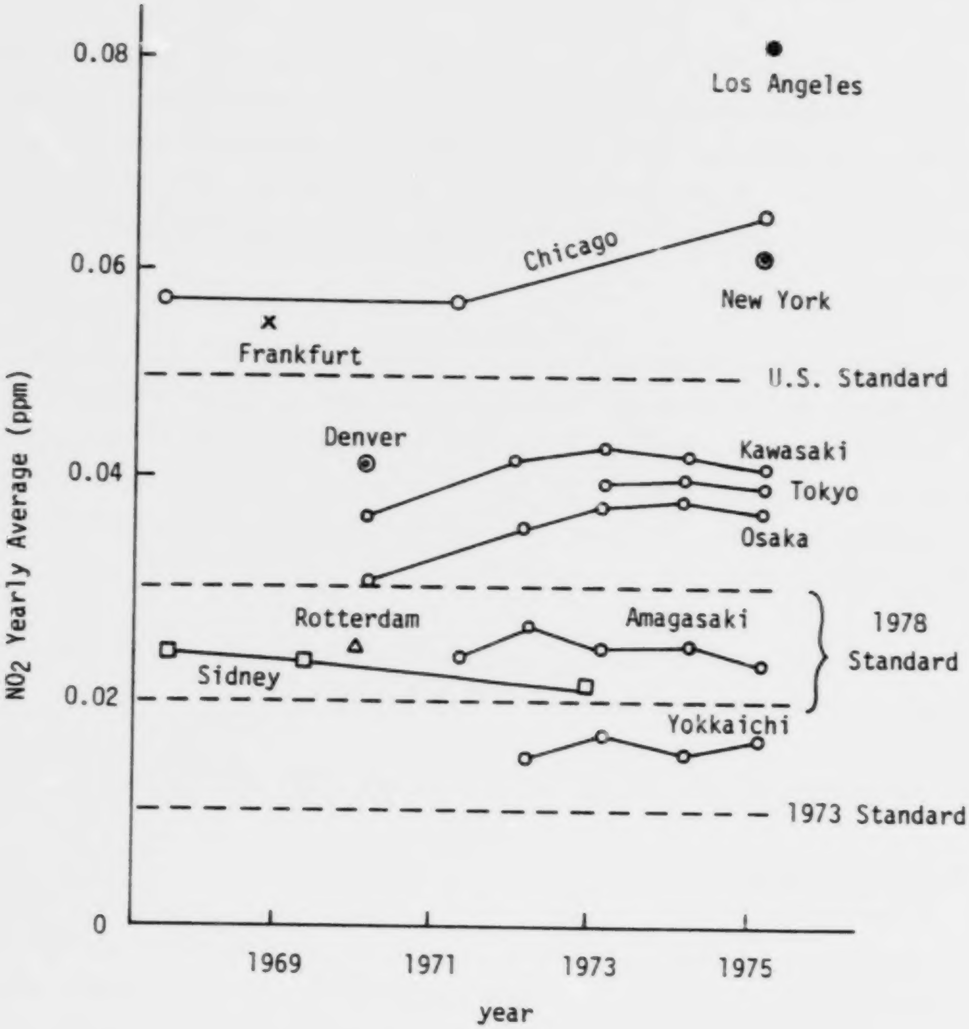

Figure 1-3. Comparison of yearly average NO_2 concentrations in major cities of the world.[2]

polluted districts, the Environment Agency also set an interim standard to be achieved in 5 years: a daily average of 0.04 ppm which is equivalent to a yearly average of 0.02 ppm.

Great efforts have been made since then to reduce NO_x emissions through combustion control, change of fuel, and flue gas denitrification at many stationary sources; and also through quite stringent regulations on automobile exhausts. It has been quite difficult, however, to achieve not only the final goal, but also the interim standard in large cities with many automobiles.

Recent studies by the Environment Agency have shown that the large safety factor which resulted in the 1973 standard (a daily average of 0.02 ppm NO_2) may not be necessary to protect human health. On the basis of a report by the Central Council for the Control of Environmental Pollution, the Environment Agency promulgated a revised NO_2 ambient standard in July 1978--a daily average of 0.04 to 0.06 ppm.

The following sections will describe various aspects of NO_x abatement, including the background of the revision of the standard.

1.2 NO_x EMISSIONS, NO_2 AMBIENT CONCENTRATIONS, AND ABATEMENT

1.2.1 NO_x Emissions

Figure 1-4 shows NO_x emissions from large stationary sources in Japan in 1975; the sources, which were controlled by emission standards, emitted a total of 920,000 tons NO_x.* Total NO_x emissions from all stationary sources, including small uncontrolled ones, are estimated at 1 million tons. NO_x derived from mobile sources is roughly estimated at about 600,000 tons yearly.

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* A metric ton equals 2,200 lbs.

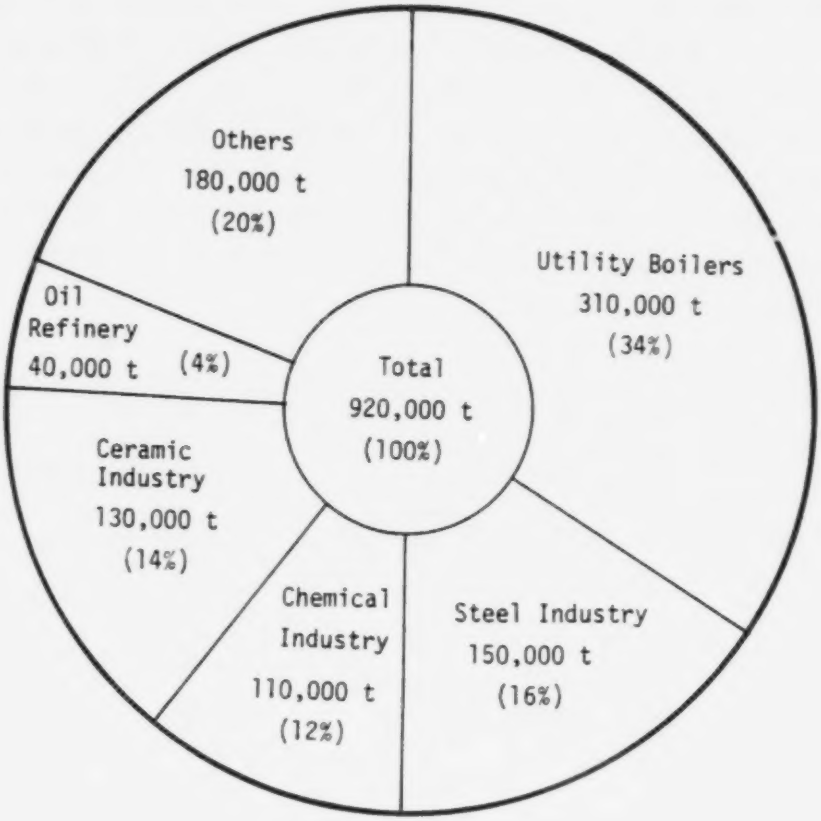

Figure 1-4. NO_x emissions from Japanese stationary sources controlled by regulation in 1975.[1]

Table 1-1 shows NO_x emissions from stationary sources in 4 regions. Region A includes 6 subregions: the 5 largest cities (Tokyo, Osaka, Yokohama, Nagoya and Kobe), including industrial areas in and around the cities, and the largest industrial complex in the Chiba-Ichihara district. Region A has the highest NO_2 concentrations, a daily average over 0.08 ppm; about 250,000 tons of NO_x were emitted there in 1975. Region B includes 9 medium size cities with total emissions of 70,000 tons and a daily average of 0.06-0.08 ppm. Region C, which includes 32 subregions (mainly smaller cities), has NO_x emissions of 190,000 tons and a daily average of 0.04-0.06 ppm. Region D contains the remaining 72 subregions and has 410,000 tons of emissions; its ambient NO_2 concentration, however, is low because it is much larger than the other regions.

TABLE 1-1. AMBIENT NO_2 CONCENTRATIONS AND EMISSIONS IN 1975 FROM STATIONARY SOURCES IN FOUR REGIONS

Region	NO_2 (ppm, daily average)	NO_x from Stationary Sources (1000 tons)	(percent)
A	Over 0.08	250	27.0
B	0.06-0.08	70	7.7
C	0.04-0.06	190	20.7
D	Below 0.04	410	44.6
Total		920	100.0

A - Largest Cities and Industrial Complexes
B - Medium Size Cities
C - Smaller Cities
D - All Others

Figure 1-5 shows the contribution of NO_x sources to ground level NO_2 concentrations. The NO_x sources include large, controlled stationary sources, mobile sources, and small uncontrolled stationary sources in each region. Over 50 percent of NO_2 is derived from mobile sources in regions A, B, and C.

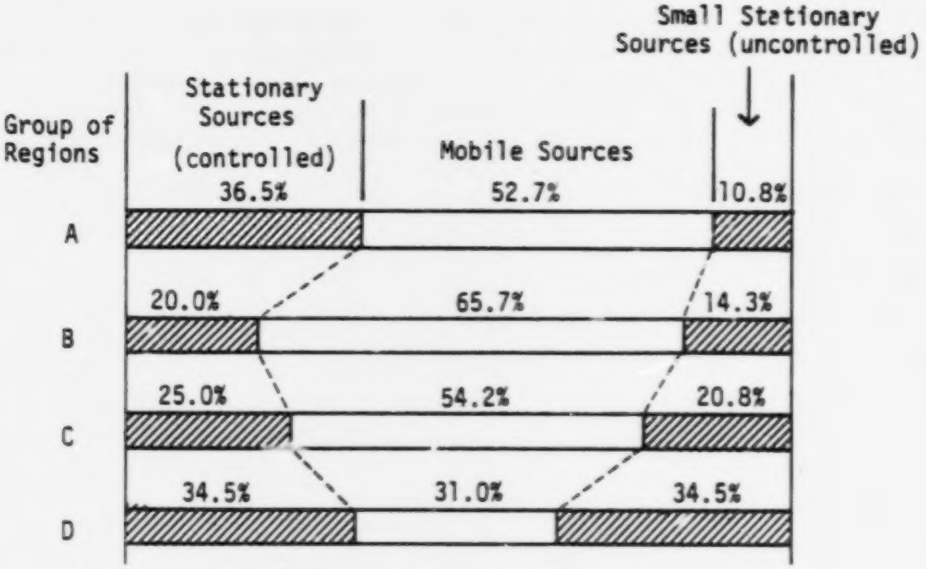

Figure 1-5. Contribution of NO_x sources to ground level NO_2 concentrations.[1]

1.2.2 Ambient NO_2 Concentrations and Abatement Standards

Ambient NO_2 concentrations have been monitored in 1975 at 666 stations scattered over Japan. (This figure does not include roadside stations to monitor automobile exhaust gas.) Annual changes in ambient NO_2 concentrations at continuous monitoring stations are shown in Table 1-2. The concentrations have remained at almost the same level or have improved slightly since 1973. The ambient NO_2 standards set in 1973 were satisfied at 4 of the total 288 stations in 1973, at 25 of the 448 in 1974, and at 54 of the 666 in 1975.

TABLE 1-2. AMBIENT NO_2 CONCENTRATIONS

Fiscal Year	Average of Annual Averages at 6 Monitoring Stations* (ppm)	Average of Annual Averages at 16 Monitoring Stations** (ppm)
1968	0.025	
1969	0.025	
1970	0.028	0.025
1971	0.026	0.024
1972	0.029	0.023
1973	0.034	0.028
1974	0.033	0.030
1975	0.030	0.030

* Tokyo, Kawasaki, Osaka, Amagasaki, Ube, and Kitakyushu.
** Six stations in Tokyo, one each in Ichihara (Chiba), Kawasaki, Nagoya, Osaka, Amagasaki, Himeji, Matsue, Kurashiki, Ube, Kitakyushu.

Figure 1-6 shows the daily average NO_2 concentrations in 80 areas of the 120 city areas and the percent of NO_x abatement required to reduce ambient NO_2 concentrations to different levels. The abatement ratios were calculated with two assumptions: 1) a proportional relationship between the amount of NO_x discharged and the ambient concentrations and 2) a background NO_2 concentration of 0.01 ppm, including NO_2 from small stationary sources not subject to regulations.

The ambient NO_2 concentration is high in large cities, and the daily average exceeds 0.08 ppm in six areas: 1) Tokyo, 2) Yokohama and Kawasaki, 3) Osaka and Sakai, 4) Nagoya, 5) Kobe and Amagasaki, and 6) Chiba and Ichihara (Region A of Table 1-1 and Figure 1-5). It is necessary in those areas to reduce NO_x by 80-90 percent to achieve the 1973 standard (0.02 ppm), 60-70 percent to achieve the interim objective (0.04 ppm), and 30-50 percent to attain the new standard (0.06 ppm). For areas in which the NO_x

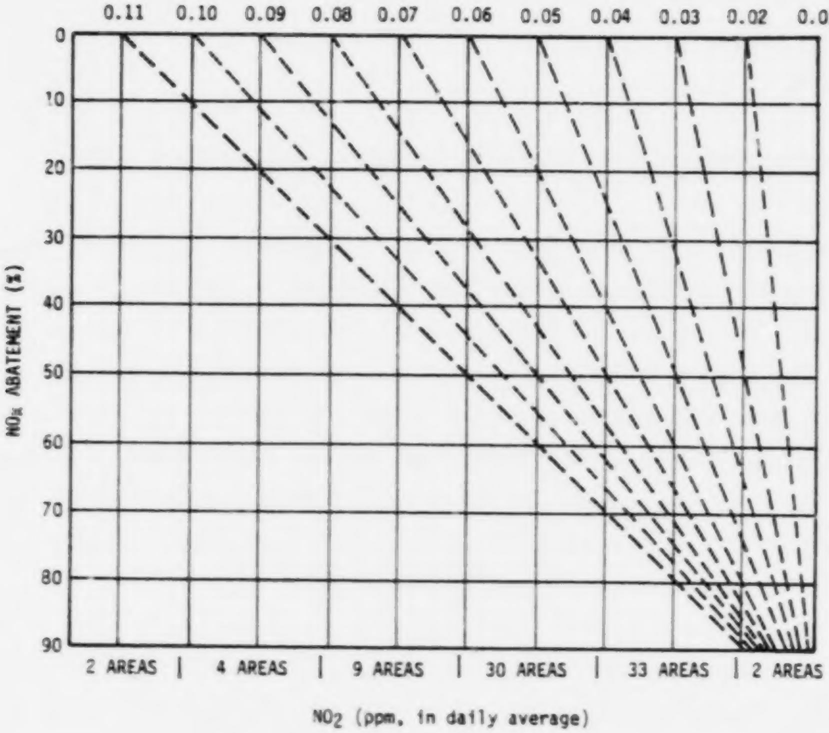

Figure 1-6. 1975 ambient NO_2 concentrations and the decrease by NO_x abatement for 80 areas of the 120 city areas.

Remarks: 1) Of the 120 areas specially designated under the Enforcement Ordinance for the Air Pollution Control Law, 80 areas having more than 2 available stations are listed in this table.

2) The background concentration is assumed to be 0.01 ppm (including smaller NO_x sources that are not subject to regulations).

concentration range is 0.06-0.08 ppm, up to 30 percent abatement is needed to achieve 0.06 ppm.

The Environment Agency has promulgated stringent regulations on automobile emissions and stationary sources in order to reduce NO_x as much as possible.

1.3 REINFORCEMENT OF NO_x EMISSION CONTROL FOR PASSENGER CARS[2]

In December 1976, the 1978 Control designed to strengthen the discharge limitations for nitrogen oxides from passenger cars, trucks and buses was announced. In response to this announcement, the Safety Standards for Vehicles for Road Transportation were partly modified by the Ministry of Transportation; the modified safety standards were to be enforced as of April 1978 on new models and March 1979 on existing models of which production is to be continued. These modified standards are shown in Table 1-3, along with the standards for 1973, 1975, and 1976; Table 1-4 presents automobile emission data for the United States.

NO_x discharge is stipulated to be less than 0.25 g/km, on the average, by 10 modes test. Accordingly, permissible limits are set at 0.48 g/km, as shown in Table 1-3. The regulations are much more stringent than those in the U.S. (Table 1-4). At the same time, those in 11 modes are strengthened, establishing the limits at 6.0 g/test (average discharge: 4.4 g/test). These modified standards are expected to contribute to a 60-70 percent reduction in NO_x discharge compared with the current regulations and to a 92 percent reduction compared with the time when there were no regulations.

Incidentally, it has thus far been believed that performance and fuel economy would decline measurably as the result of an attempt to reduce NO_x discharge. Strenuous efforts were made, however, to maintain and even to improve fuel economy while preserving performance to an extent that no problems should occur in practical use in spite of the modified standards.

TABLE 1-3. STANDARDS FOR AUTOMOBILE EMISSIONS IN JAPAN*

	HC (g/km, 10 modes)	CO (g/km, 10 modes)	NO_x (g/km, 10 modes)
1973	3.80 (2.94)	28.00 (18.40)	3.00 (2.18)
1975	0.39 (0.25)	2.70 (2.10)	1.60 (1.20)
1976	0.39 (0.25)	2.70 (2.10)	0.84 (0.60)
1978	0.39 (0.25)	2.70 (2.10)	0.48 (0.25)

* Figures show allowable limits; those in parentheses show average emissions.

TABLE 1-4. STANDARDS FOR AUTOMOBILE EMISSIONS IN THE UNITED STATES*

	HC (g/km)	CO (g/km)	NO_x (g/km)
1978	0.94	9.4	1.25
1979	0.94	9.4	1.25
1980	0.26	4.4	1.25
1981	0.26	2.1	0.63

* Established by the Clean Air Act of 1977.

As a result of these efforts, fuel consumption of automobiles which conform to the 1976 Control has been improved to the extent that there is no noticeable decline compared with those conforming to the 1974 Control. On the contrary, improvements have been made in the case of some types of automobiles.

Fuel consumption rates have also been considerably improved in systems where NO_x discharge limits of 0.25 g/km were satisfied. Performance better than that of automobiles conforming to the 1976 Control has been observed in most of the cases. It should be noted that a new combustion method has made the fuel consumption rates of some models even better than those of automobiles in conformity with the 1973 Control.

It was decided that the regulations for trucks and buses should be reinforced with the control measures presently available and within the scope that could be achieved in a limited time period. In December 1976, reinforced regulations were announced as the 1977 Control for trucks and buses. This announcement was made simultaneously with the announcement of the reinforced regulations for passenger cars. These tightened regulations provide that the discharge of NO_x from diesel-engined vehicles should be reduced by approximately 30 percent as compared with the time when there were no such regulations; the discharge from heavier gasoline-engined cars and LPG-engined cars is to be reduced by approximately 47 percent.

It is estimated, however, that the total amount of NO_x discharged from from automobiles will remain at somewhere around 66 percent of that in 1975, including a 10 percent reduction through traffic control, even in the year 1983 when the control measures are expected to exhibit their maximum effect (see Figure i-7).

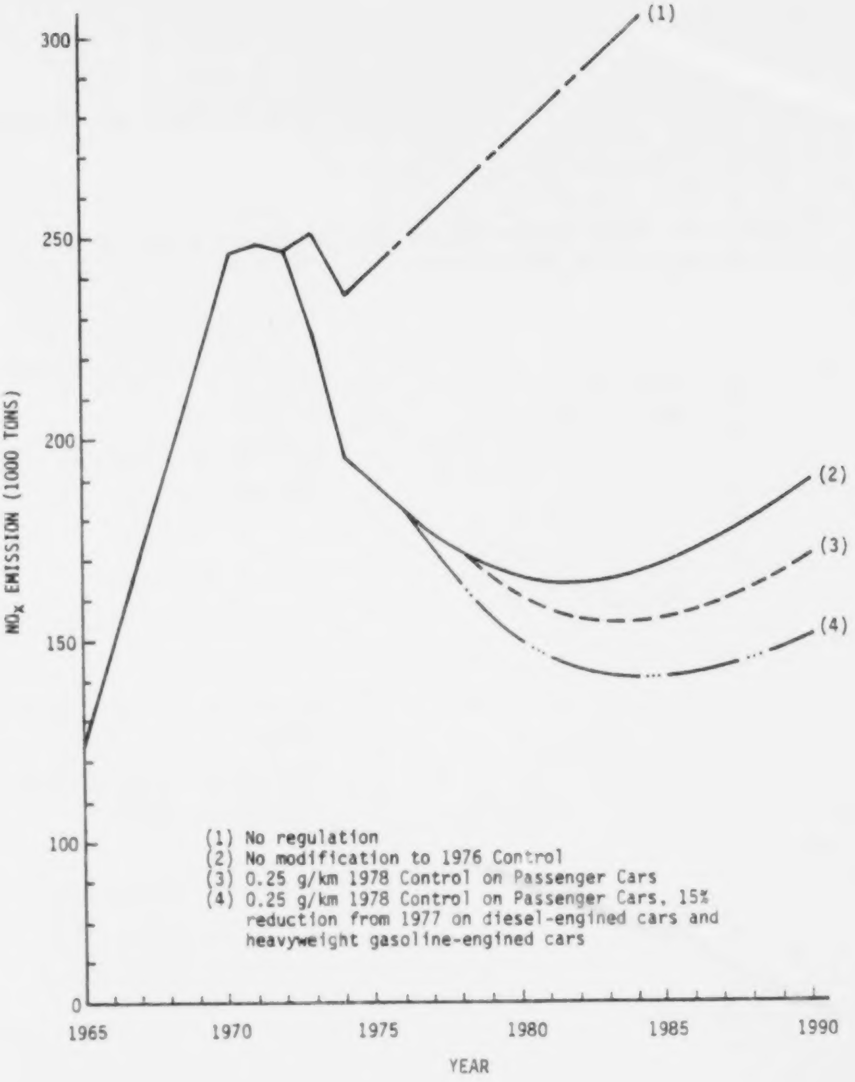

Figure 1-7. Estimated total amount of NO$_x$ emissions from road traffic in the Tokyo Bay Area.[2]

1.4 COUNTERMEASURES FOR STATIONARY SOURCES

1.4.1 Methods of NO_x Abatement

Major methods of NO_x abatement for stationary sources are classified in Table 1-5.

TABLE 1-5. CLASSIFICATION OF NO_x ABATEMENT METHODS

Reduction of Formation	Combustion Modification	Low Oxygen Combustion
		Flue Gas Recirculation
		Staged Combustion
		Off-Stoichiometric Combustion
		Low-NO_x Burners
	Use of Low-Nitrogen Fuel	Change of Fuel
		Nitrogen Removal from Fuel
NO_x Removal from Flue Gas	Dry Process	Selective Catalytic Reduction (SCR)
		Selective Noncatalytic Reduction (SNR)
	Wet Process	Oxidation Absorption
		Oxidation Reduction
		Absorption Reduction

Combustion modification is the most reasonable primary step of abatement. (It will be described in Chapter 2.) Combustion modification has been widely applied in Japan and has contributed to 10-60 percent of NO_x abatement for each source.

The change from high-nitrogen to low-nitrogen fuel has also been carried out to a considerable degree. Heavy oil, the major fuel in Japan, contains 0.2-0.3 percent nitrogen, and the combustion gas contains 110-130 ppm of NO_x under the best combustion control. A considerable number of new power plants burn LNG (imported liquid natural gas), which yields only 35 ppm of NO_x under the best combustion control. There is, however, a limit to the supply of such clean fuel, and it is costly. Hydrodesulfurization of heavy oil, which removes 70-90 percent sulfur, also removes 20-30 percent nitrogen, but this does not reduce NO_x substantially.

In order to remove NO_x present in flue gas, many processes of denitrification have been developed. Of these, selective catalytic reduction (SCR) that uses NH_3 and a catalyst to reduce NO_x to N_2 at 200-400°C has been the most widely employed: it is simple, has a high (90 percent) NO_x removal efficiency, and does not produce by-products difficult to dispose of. Although NO_x can be reduced to N_2 by other reducing gases such as H_2, CO and CH_4, large amounts of these gases are consumed by reacting with the O_2 in flue gas. The use of NH_3 is more suitable because it selectively reacts with NO_x (see Chapter 3).

Selective noncatalytic reduction (SNR, NH_3 reduction without a catalyst) has been used in several plants. SNR is much simpler than SCR, but the NO_x removal efficiency does not exceed 50 percent and a considerable amount of NH_3 is emitted (see Chapter 5).

Both SCR and SNR consume ammonia--0.8-1.2 moles of NH_3 to every mole of NO_x for SCR and 1.5-2.5 moles for SNR. It is possible that when SCR and SNR are applied widely in many countries, ammonia will fall into short supply; as a result, supplies of nitrogen fertilizer and food will be affected. Therefore, it is desirable that processes that do not consume ammonia be developed.

Most wet processes do not consume ammonia. Some of them even convert NO_x to NH_3. The wet processes, however, are not as simple as SCR or SNR and moreover, present wastewater treatment problems (Chapter 7).

1.4.2 Emission Standards

The first regulations governing emission standards for nitrogen oxides from stationary sources were originally established in August 1973. Large boilers, heating furnaces, nitric acid manufacturing facilities and other sources were subject to the regulations in establishing the emission standards.

In 1975, standard values and expansion of the scope of facilities subject to the regulations were enforced. These second-stage regulations included medium-size facilities, as well as cement calcination furnaces and newly built coke furnaces.

Third-stage regulations were enacted in June 1977 (see Table 1-6). Their major points include expansion of the types and capacities of facilities subject to regulation, and reinforcement of the standards for newly built facilities. The standards went into effect on June 18, 1977 for facilities built after this date. In regard to the existing facilities, the regulations provide that the standards be applied as of May 1, 1980, and in principle allow for a grace period of three years. Also, the standards are expected to be applied as of October 1, 1980, to liquid combustion boilers of between 5000 and 10,000 Nm^3/hr emission gas; this takes into consideration the period required for measuring NO_2 concentrations and other factors.

Less stringent standards are applied to existing boilers with an FGD system (Table 1-7). Boilers to be constructed, however, are subject to uniform NO_x regulations regardless of whether they are equipped with an FGD plant.

TABLE 1-6. NO_x EMISSION STANDARDS FOR STATIONARY SOURCES (PPM)

Sources	Capacity, (1000 Nm^3/hr)	New Plants			Existing Plants			O_2 in Gas (%)
		1977	1975	1973	1977	1975	1973	
Boiler (Gas-Fired)	More than 500	60	100	130	130	130	170	5
	100-500	100	100	130	130	130	170	
	40-100	130	130	130	130	130	n	
	10-40	130	130	n	150	150	n	
	5-10	150[b]	n	n	150[a]	n	n	
	Less than 5	150[b]	n	n	n	n	n	
Boiler (Coal-Fired)	More than 100	400	480	480	480	600	750	6
	40-100	400	480	480	600	750	n	
	10-40	400	480	n	600	750	n	
	5-10	400[b]	n	n	480[a]	n	n	
	Less than 5	400[b]	n	n	n	n	n	
Boiler (Oil-Fired)	More than 500	130	150	180	180	230	230	4
	100-500	150	150	180	190	230	230	
	40-100	150	150	180	190	190	n	
	10-40	150	150	n	230	n	n	
	5-10	180[b]	n	n	250[a]	n	n	
	Less than 5	180[b]	n	n	n	n	n	
Iron Ore Sintering Machine	More than 100	220	n	n	260	n	n	15
	Less than 100	230	n	n	270	n	n	
Alumina Calciner	More than 10	220	n	n	n	n	n	10
Metal Heating Furnace	More than 100	100	100	200	160	220	220	11
	40-100	130	150	200	170	220	220	
	10-40	130	150	170	200	n	n	
	5-10	150	n	n	n	n	n	
	Less than 5	180	n	n	n	n	n	
Oil Heating Furnace	More than 100	100	100	170	170	210	210	6
	40-100	100	100	170	170	210	210	
	10-40	130	150	170	180	n	n	
	5-10	150	n	n	n	n	n	
	Less than 5	180	n	n	n	n	n	
Cement Kiln	More than 100	250	250	n	480	n	n	10
	Less than 100	350	n	n	480	n	n	
Coke Oven	More than 100	170	200	n	350	n	n	7
	Less than 100	170	n	n	350	n	n	
Waste Incinerator	More than 40	250	n	n	n	n	n	12

[a] Must be met by October 1, 1980.

[b] For plants to be constructed after September 10, 1977.

n = No regulation.

TABLE 1-7. NO_x EMISSION STANDARDS FOR EXISTING OIL-FIRED BOILERS WITH AND WITHOUT FGD SYSTEMS (PPM)

	Capacity (1000 Nm^3/hr)				
	More than 1000	500-1000	40-500	10-40	5-10
Without FGD	180	180	190	230	250
With FGD	180	210	210	250	280

The third-stage emission standards may be the most stringent at the present in the world; nevertheless, it is possible to achieve them with the most advanced technology of combustion modification, including the use of low NO_x burners and the switching of fuels to some extent.

It is expected that the third-stage regulations will result in a reduction of NO_x emissions of approximately 8 percent as compared with those of 1975 and a cumulative reduction of approximately 30 percent as compared with the value at the time of the first regulations. Even with these efforts, it is not possible in many regions to attain even the interim objective of the 1973 standard, a daily average of 0.04 ppm.

1.5 COST ESTIMATES FOR NO_x ABATEMENT FOR STATIONARY SOURCES AND LIMIT OF ABATEMENT

1.5.1 Estimate by MITI[3]

The Ministry of International Trade and Industry (MITI) has made cost estimates for NO_x abatement to reach different ambient NO_2 concentrations ranging from 0.02 to 0.07 ppm in daily average. For convenience, the whole of Japan was divided into four regions:

- Region I - Large cities such as Tokyo, Osaka, and Nagoya that account for one-third of Japan's total population.

- Region II - Forty-three industrial complexes that include Kashima, Mizushima, and Kitakyushu.

- Region III - Eighty-six local cities, including Sapporo.

- Region IV - Other areas.

NO_x abatement required for stationary sources to reach different NO_2 levels in 1985 and methods for the abatement are shown in Table 1-8 and 1-9, respectively.

It has been assumed that SCR was used for NO_x removal from flue gas, because it is the most practical method at present. The investment costs for SCR plants with different capacities for clean and dirty gases are shown in Figure 1-8.* The plants are for existing boilers and treat clean gas after it has passed through a preheater or dirty gas after FGD. The investment costs are rather high because those were estimated with enough safety margin to ensure trouble-free operation. Utility requirements for an SCR unit with a capacity of treating 200,000 Nm^3/hr of flue gas (66 MW equivalent) are as follows assuming operation for 70 percent of the total hours of a year:

Power: 7.67×10^6 kWhr/year
Fuel for gas heating: 3.07×10^3 kl/year
Ammonia: 251 tons/year (at 300 ppm NO_x in gas, 0.9 mole NH_3/ mole NO_x for about 85 percent removal).

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* Clean gas is gas that is free of SO_x and particulates, but does contain NO_x; dirty gas contains SO_x and particulates in addition to NO_x.

TABLE 1-8. NO_x ABATEMENT NEEDED TO REDUCE AMBIENT NO_2 CONCENTRATION TO DIFFERENT LEVELS IN 1985

NO_2 Daily Average (ppm)	Abatement Required (percent)			
	I	II	III	IV
0.06	43	2	11	0
0.05	55	22	29	0
0.04	66	41	46	19
0.03	77	61	64	46
0.02	89	80	82	73

TABLE 1-9. METHODS OF ABATEMENT

Method	Abatement (percent)	Investment Cost ¥/Nm^3/hr (\$/Nm^3/hr)
Combustion Modification	10-40	470 (2.30)
Fuel Switching	7-39	None for User (Fuel Cost Increases)
Flue Gas Treatment	80-90	6500-18,000 (32.5-90) - Dirty Gas 3000-7500 (15-37.5) - Clean Gas (As shown in Figure 1-8)

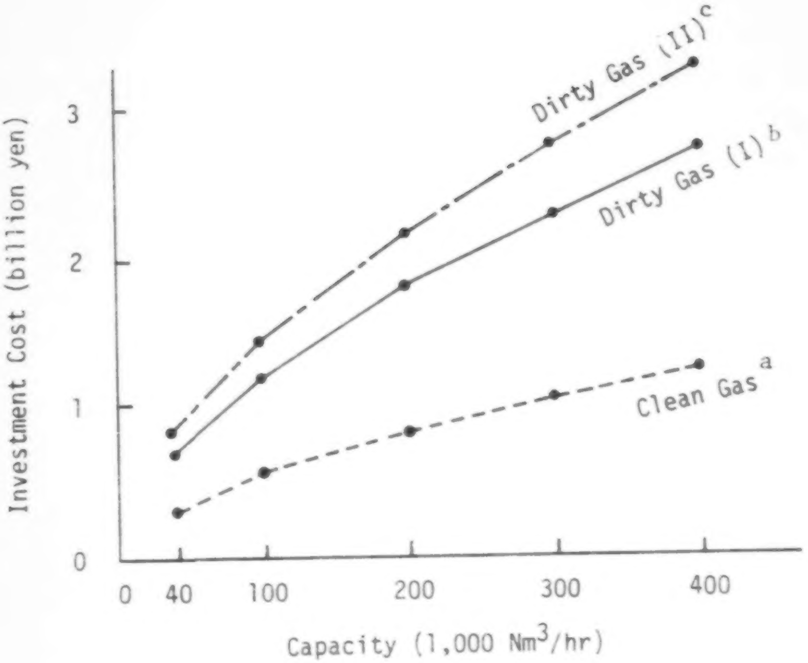

Figure 1-8. Investment costs for SCR denitrification plants estimated by MITI.

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[a] Clean Gas: From fuel gas, kerosene.

[b] Dirty Gas (I): From heavy oil burning boiler, coke oven, etc.

[c] Dirty Gas (II): From iron-ore sintering machine, coal-fired boiler, glass furnace, cement kiln, etc.

Catalyst cost was assumed at 3.5 million yen ($17,500)/m^3 of catalyst with an SV of 5000 hr^{-1} for dirty gas and 2.5 million yen ($12,500)/m^3 with an SV of 10,000 hr^{-1} for clean gas.

By flue gas treatment, about 90 percent of NO_x in the gas can be removed. However, it is not practical to apply SCR to numerous sources with a capacity smaller than 40,000 Nm^3/hr (13 MW equivalent). Even for larger sources, many sources have no room to install an SCR unit because they have already installed an FGD unit. The practical maximum amount of flue gas that can be treated is shown in Table 1-10.

TABLE 1-10. PRACTICAL AMOUNT OF FLUE GAS TO BE TREATED

NO_x Daily Average (ppm)	0.06	0.05	0.047
Gas To Be Treated (10^6 Nm^3/hr)	48	84	120

In order to reach the ambient NO_2 concentrations below 0.06 ppm, fuels must be switched from heavy to lighter oils for many of the NO_x sources for which SCR cannot be applied. Thus construction of plants to reduce the nitrogen content of heavy oil is required. To attain a daily average of 0.47 ppm in 1985, 30 million kiloliters of heavy oil should be treated during the year. This requires 26 units for heavy oil decomposition by hydrogen addition, with a total capacity of 640,000 BPSD, and 9 units for thermal decomposition (coking) with a total capacity of 220,000 BPSD.

Figure 1-9 shows the total investment costs needed between 1976 and 1985 to reach different NO_2 levels; Figure 1-10 presents the annualized costs, including 7 years depreciation, required to reach different NO_2 levels in 1985. As for the investment costs, about 0.4 trillion yen ($2 billion) is required to reach 0.06 ppm, about 1 trillion yen ($5 billion)

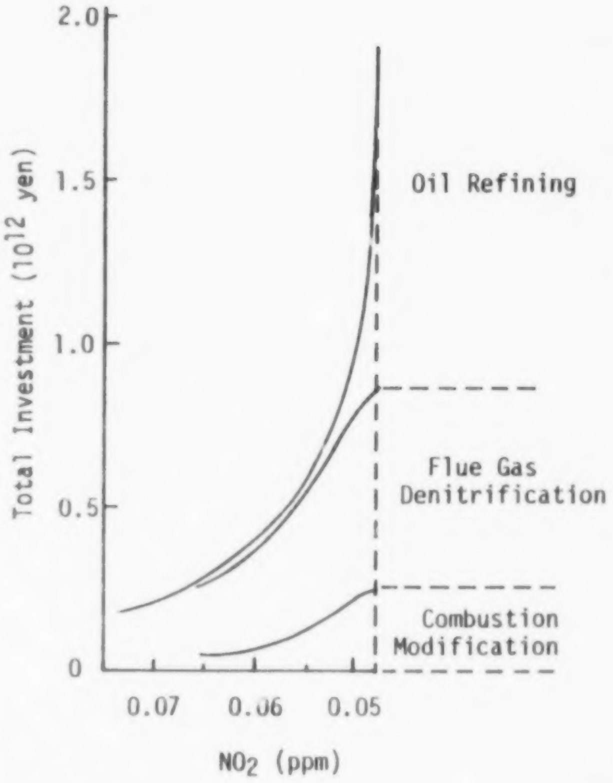

Figure 1-9. Total investment costs required between 1976 and 1985 to reach different NO_2 concentrations (daily averages).

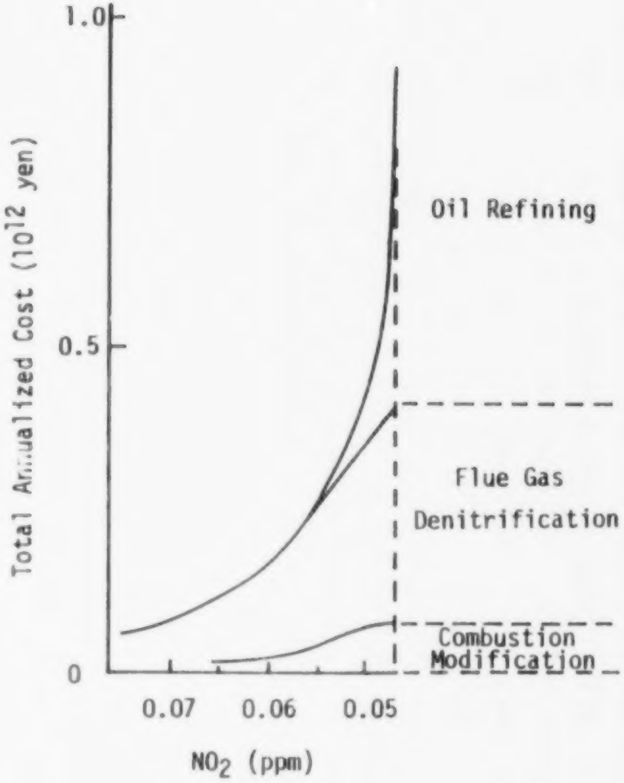

Figure 1-10. Annual costs in 1985 needed to reach different NO_2 concentrations (daily averages).

to reach 0.05 ppm, and 2 trillion yen ($10 billion) to reach 0.047 ppm. Of the 0.4 trillion yen investment required to reach 0.06 ppm, nearly 0.1 trillion yen is for combustion modification (CM) and about 0.3 trillion yen for flue gas treatment (FGT). To reach 0.047 ppm, an investment of about 1 trillion yen is required for heavy oil decomposition in addition to 0.2 trillion yen for CM and 0.7 trillion yen for FGT. Further reduction will require exceedingly large investments for heavy oil decomposition. The annual costs are about 150 billion yen ($750 million) for 0.06 ppm, nearly 500 billion yen ($2.5 billion) for 0.05 ppm, and about 1 trillion yen ($5 billion) for 0.047 ppm.

The energy requirements for NO_x abatement are shown in Figure 1-11. The energy requirements are an equivalent of 110,000 kl oil to reach 0.06 ppm, 250,000 kl to reach 0.05 ppm (mainly for flue gas treatment), and about 650,000 kl (including about 400,000 kl for heavy oil decomposition) to reach 0.047 ppm.

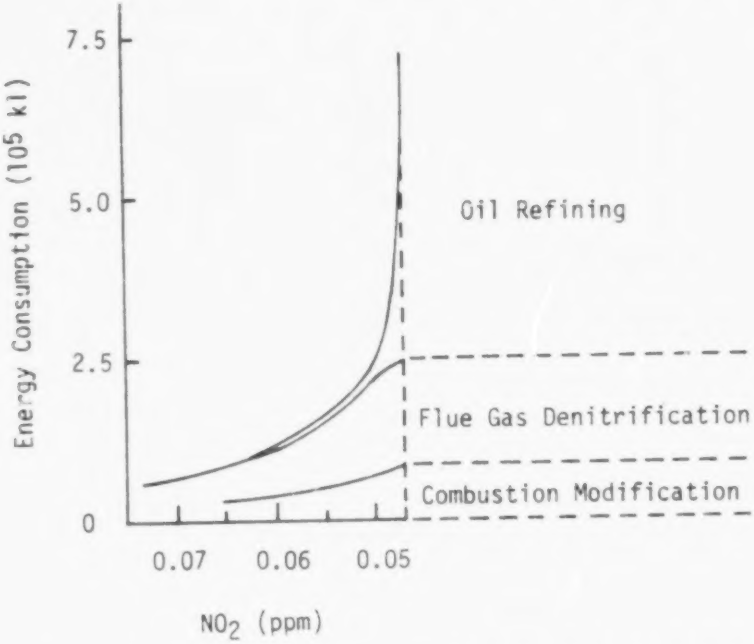

Figure 1-11. Energy consumption required in 1985 to reach different NO_x concentrations (daily averages).

These estimates indicate that cost escalates so rapidly that the practical, attainable ambient NO_2 concentration is a daily average of 0.05 ppm, which is equivalent to a yearly average of 0.025 ppm.

1.5.2 Estimates by Environment Agency[1]

The Environment Agency (EA) also estimated the cost of NO_x abatement.[3] Japan was divided into 4 regions (A, B, C and D), according to daily average NO_2 concentrations of over 0.08 ppm, 0.06-0.08 ppm, 0.04-0.06 ppm, and below 0.04 ppm, respectively (see Table 1-1). The EA assumed the following 4 cases for each region:

- Case a - Maintain the third-stage emission regulations (Table 1-6).
- Case b - Tighten the regulations for stationary sources to achieve a daily average of 0.06 ppm in 1985.
- Case c - Tighten the regulations to achieve a daily average of 0.04 ppm in 1985.
- Case d - Take all possible, practical countermeasures for stationary sources, *e.g.*, combustion modification and flue gas denitrification.

In Case a, NO_x emissions in 1985 will increase by 20 percent over 1975 due to an increase in new NO_x sources. The abatement ratios in other cases are shown in Table 1-11.

TABLE 1-11. NO_x ABATEMENT (PERCENT) FOR STATIONARY SOURCES IN 1985

	Region A	Region B	Region C	Region D
Case b	40	17	0	0
Case c	64	50	21	0
Case d	76	66	47	0

For the abatement in 1985, the methods of abatement were assumed to be combustion modification (an average abatement of 30 percent), flue gas denitrification by selective catalytic reduction (90 percent abatement), and selective noncatalytic reduction (50 percent abatement). The estimated total investment costs between 1975 and 1985 and the annual costs in 1985, including 7 years depreciation, fuel for gas reheating, etc., are shown in Figure 1-12.

NO_x emissions from stationary sources in 1985 and the percents of investment costs for combustion modification, SCR and SNR in each case are shown in Table 1-12. In Case a, 68 percent of the total investment is for combustion modification; in Case d, however, 15 percent is for combustion modification, while 75 percent is for SCR and 10 percent for SNR. This means that all possible combustion modification is done in Case a, but in other cases flue gas denitrification, particularly SCR, is increasingly used.

The investment cost for each industry is shown in Table 1-13. The power industry requires large investments, for example, 283.8 billion yen in Case d. Tht total power generation capacity in Japan in 1985 is estimated to be 200,000 MW, about half of which is thermal (steam) power.

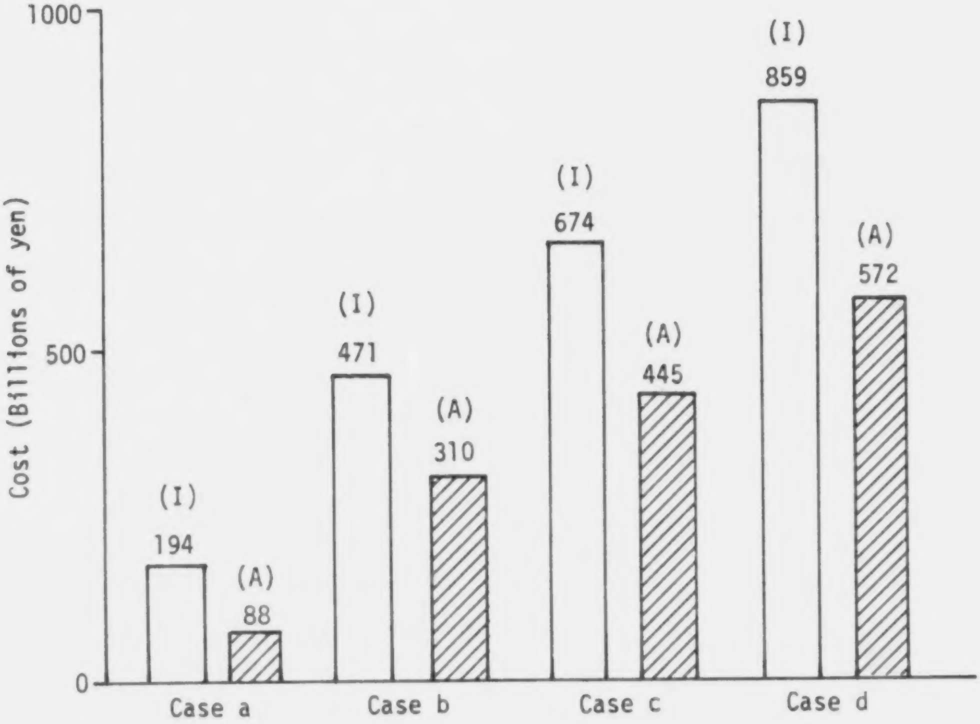

Figure 1-12. Investment cost (I) and annual cost (A) for each case.

TABLE 1-12. NO_x EMISSIONS IN 1985 AND THE PERCENT OF INVESTMENT COSTS FOR EACH COUNTERMEASURE

	Case a	Case b	Case c	Case d
NO_x Emissions (1000 t)	1108	800	679	600
Combustion Modification (Percent)	68	22	19	15
SCR (Percent)	18	52	65	75
SNR (Percent)	14	21	16	10
Total (Percent)	100	100	100	100

TABLE 1-13. INVESTMENTS FOR NO_x ABATEMENT BY INDUSTRIES (Billions of Yen)

	Case a	Case b	Case c	Case d
Power	66.4	187.0	240.0	283.8
Steel	48.1	75.2	91.0	134.8
Chemical	15.6	37.1	59.9	98.0
Cement	7.8	26.0	31.6	35.9
Glass	0.0	0.2	0.9	2.6
Oil Refining	7.0	15.6	18.1	36.9
Other	49.4	129.8	232.5	267.1
Total	194.3	470.9	674.0	859.1

Figure 1-13 shows ambient NO_2 concentrations in each region in 1975 and in cases a, b, c and d for each region in 1985. In addition to the control of stationary sources, passenger cars are controlled by the 1978 regulation and buses and trucks by the 1979 regulations. In case d in 1985, the concentration is reduced to 0.03 ppm in Regions C and D but exceeds 0.04 ppm in Region A. To reduce NO_x further, many plants for heavy oil composition are needed. Since the construction of many decomposition plants is not practical due to high costs, attainment of the interim objective of the 1973 standard--a daily average of 0.04 ppm--may be practically impossible in Region A.

This conclusion is similar to that obtained by MITI (Section 1.5.1), except that EA's cost estimates for NO_x abatement for stationary sources are about half of those estimated by MITI. EA's cost estimate for SCR is much lower than MITI's (Section 3.6.2). The low cost may be due primarily to the recent progress in SCR by which flue gas from the boiler economizer containing large quantities of SO_x and fly ash can be directly treated. It may be based partly on the recent unusually low costs offered by plant constructors due to excessive competition. MITI's cost estimate for SCR may be based on the actual high cost in the past, including heating facilities for the cooled gas. The real cost for NO_x abatement may be between the costs estimated by MITI and EA.

1.6 REVISION OF AMBIENT NO_2 STANDARD

1.6.1 Consultation for Criteria and Guidelines for NO_2 That Has Adverse Effects on Human Health

The ambient air quality standard for NO_2, established in 1973, was based on limited data and information available prior to June 1972. The standard allowed for a sufficient safety factor with a view to nipping pollution problems in the bud. Considerable amounts of data were made available through biological experiments; on the other hand, epidemiological

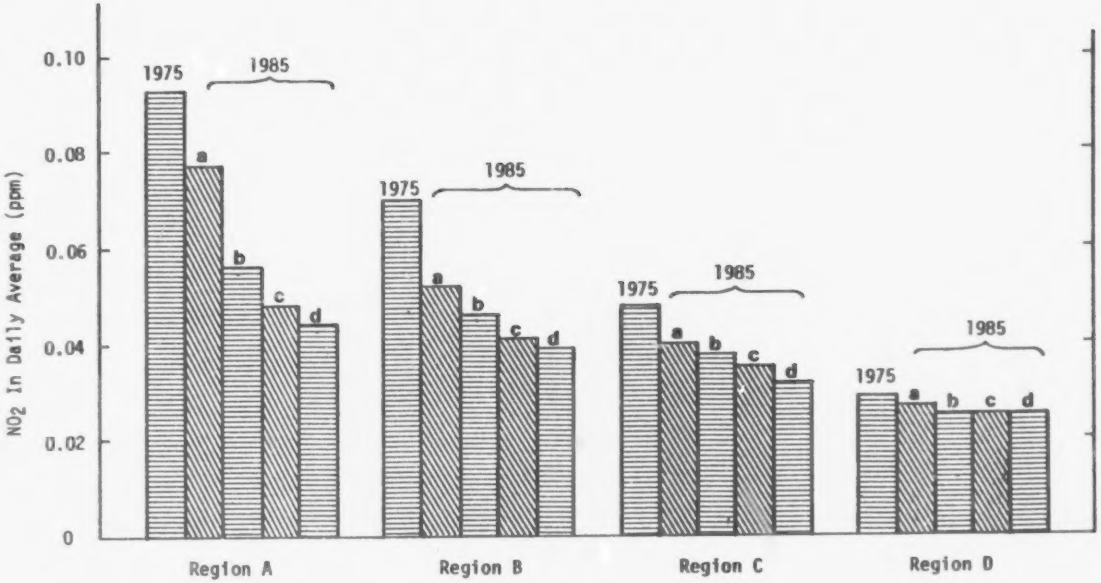

Figure 1-13. Ambient NO_2 concentrations in 1975 and 1985 with countermeasures a, b, c and d.[1]

data were scarcely available in Japan or in other countries. Five years have passed, and some scientific data and information have been obtained since then.

A meeting of an expert committee of the World Health Organization (WHO) was held in Tokyo in August 1976; the one-hour NO_2 value of 0.5 ppm was established as the threshold. Using a safety factor of 3-5, WHO suggested a one-hour NO_2 value of 0.10-0.17 ppm as a criterion.

Also, a population-based survey of the influence of combined air pollution on health was carried out as part of an epidemiological study on the adverse effects of ambient air pollution on the public health of communities. The results were made public in January 1977.

The Basic Law for Environmental Pollution Control stipulates that scientific consideration shall always be given to any environmental quality standard. Since much more data and information became available in Japan, as well as from other countries, more accurate criteria were to be established. In light of this, the Central Council for the Control of Environmental Pollution was consulted in March 1977 about criteria and guidelines concerning the adverse effects of NO_2 on human health and the establishment of acceptable as well as desirable levels.

1.6.2 New NO_2 Standard

In March 1978, the Council recommended the following NO_2 criteria: a yearly average of 0.02 to 0.03 ppm and an hourly average of 0.1 to 0.2 ppm. These values are close to those given by the OECD experts.

In July 1978, EA promulgated an amended NO_2 ambient standard, a daily average of 0.04 to 0.06 ppm. In regions where the daily NO_2 average concentration exceeds 0.06 ppm, the concentration is to be reduced to 0.06 ppm in 7 years. In regions where the NO_2 concentration ranges between 0.04 and

0.06 ppm, efforts shall be made to keep the NO_2 concentration from exceeding the present level appreciably. In regions where the NO_2 concentration is below 0.04 ppm, efforts shall be made to keep it from exceeding 0.04 ppm appreciably.

It may be unusual for an air quality standard to prescribe a range of concentrations. Presumably EA wanted to set the standard at 0.04 ppm, the interim objective of the 1973 standard, because some of the local governments had been trying to reduce NO_2 concentrations to 0.04 ppm. This level, however, has been practically impossible to attain in large cities where most of the NO_x is derived from mobile sources and numerous small uncontrollable stationary sources. For human health, 0.06 ppm is considered acceptable, but a lower level is obviously desirable. The new standard with a range of concentrations has been set under such circumstances.

EA is going to set a total mass NO_2 regulation for regions in which NO_2 concentration exceeds 0.06 ppm in order to reduce the concentration to 0.06 ppm within 7 years. A considerable number of flue gas denitrification plants will be required to meet the total mass regulation.

Some of the local governments which had made efforts to attain 0.04 ppm are not satisfied with the new standard and plan to continue to strive for that level. This effort will require very stringent NO_x control of new large plants; it may even necessitate the construction of flue gas denitrification plants in less polluted regions.

EA has continued to use the Saltzman process as the official analytical method for the measurement of ambient NO_2 concentration. The factor for the calculation of NO_2 concentration has been revised from 0.72 to 0.84. This factor change has resulted in a slight relaxation of the NO_2 standard.

1.7 NO_x ABATEMENT BY INDUSTRIES

1.7.1 Introduction

In Japan, the largest stationary source of NO_x is the power industry, which annually emits 310,000 tons of NO_x. Thus, this industry accounts for 34 percent of the total emissions from stationary sources (Figure 1-4). The second largest source is the steel industry, which emits 150,000 tons (16 percent), and the third is the ceramic industry, which emits 130,000 tons (14 percent).

The power companies have concentrated their efforts mainly on combustion modification and recently constructed several large test plants and commercial plants for denitrification.

The steel industry has been most active in developing flue gas denitrification technology, because combustion modification is not useful for flue gas from iron-ore sintering machines, the major gas source at steel works.

The ceramic industry has also conducted pilot plant tests in an attempt to reduce NO_x. Flue gases from cement kilns and glass furnaces are difficult to treat by selective catalytic reduction because they contain considerable amounts of particulates and alkaline vapor.

Efforts for NO_x abatement by these industries will be briefly reviewed next.

1.7.2 NO_x Abatement for Utility Boilers

Utility power companies have made concerted efforts for NO_x abatement mainly by combustion modification and change of fuels. Consequently, the emission standards have been more than adequately met. For example, flue gas from new LNG-fired boilers contains only 35-50 ppm of NO_x, while the emission standard is 100 ppm. Flue gas from existing oil-fired boilers contains 100-130 ppm of NO_x.

However, local governments usually impose much more stringent regulations for the construction of new power plants. This necessitates flue gas denitrification facilities. The power companies have made extensive tests on flue gas denitrification with many pilot and prototype plants.

Table 1-14 lists major flue gas denitrification test plants and commercial plants of power companies. Since NO_x concentration is reduced to a low level by combustion modification, 40-80 percent NO_x removal by flue gas denitrification is sufficient.

Several new coal-fired utility boilers are under construction or in the planning stage. Usually coal-fired boilers are installed in locations considerably distant from cities. Although the NO_x concentration of flue gas is reduced to 200-300 ppm by combustion control, some boilers may require a flue gas denitrification plant.

Most of the plants use SCR (selective catalytic reduction). SNR (selective noncatalytic reduction) has been used in one plant at Chita station, Chubu Electric, but the NO_x removal efficiency is only about 45 percent, with an outlet NH_3 of 20-30 ppm. Large scale tests of the SNR-SCR combination have been started at three power stations by Companies B, E and F (the names are confidential). Their aim is to increase the NO_x removal efficiency to 50-60 percent and to decrease the outlet NH_3 to 10 ppm by placing a small amount of SCR catalyst in a duct between the boiler economizer and air preheater.

TABLE 1-14. TEST AND COMMERCIAL PLANTS FOR UTILITY BOILERS (LARGER THAN 280,000 Nm^3/hr)

Power Company	Plant Site	Fuel	Capacity MW	Capacity 1000 Nm^3/hr	Plant Constructor	Process	Completion	NO_x Removal (%)
Chubu Electric	Chita	Low-S Oil	375	1036	MHI[a]	SNR[b]	Feb 1977	45
Chubu Electric	Chita	LNG	700	1910	Hitachi, Ltd.	SCR[c]	Apr 1978	80
Chubu Electric	Chita	LNG	700	1910	Hitachi, Ltd.	SCR	Sept 1978	80
Chubu Electric	Chita	Low-S Oil	700	1920	MHI	SCR	Feb 1980	80
Kansai Electric	Kainan	Low-S Oil	115	300	Hitachi, Ltd.	SCR	June 1977	80
Company A	--	Low-S Oil	156	490	Hitachi, Ltd.	SCR	June 1978	50[g]
Company B	--	Low-S Oil	175	550	Hitachi, Ltd.	SNR+SCR[e]	June 1978	50[g]
Kyushu Electric	Kitakyushu	LNG	600	1610	MHI	SCR	July 1978	80
Kyushu Electric	Kitakyushu	LNG	600	1610	MHI	SCR	Dec 1978	80
Company C	--	Low-S Oil	375	1010	MHI	SCR	Feb 1978	40[g]
Company D	--	Low-S Oil	156	490	MHI	SCR	July 1978	40[g]
Company E	--	Low-S Oil	350	1020	IHI[d]	SNR+SCR	Apr 1978	50[g]
Company F	--	Low-S Oil	156	490	IHI	SNR+SCR	June 1978	60[g]
Chugoku Electric	Kudamatsu	Low-S Oil	350	1000	IHI	SCR	Apr 1979	80
Chugoku Electric	Kudamatsu	Low-S Oil	700	1900	IHI	SCR	July 1979	80
Tohoku Electric	Niigata	Low-S Oil	600	1660	IHI	SCR	Aug 1981	60
Electric Power P.C.	Takahara	Coal	250	800	--	SCR	June 1981	(80)[h]
Hokkaido Electric	Tomakomai	Coal	350x¼[f]	280	Hitachi, Ltd.	SCR	Oct 1980	(90)[h]

[a] Mitsubishi Heavy Industries.
[b] Selective noncatalytic reduction.
[c] Selective catalytic reduction.
[d] Ishikawajima-Harima Heavy Industries.
[e] Combination of SNR and SCR
[f] One-fourth of the gas from a 350 MW boiler.
[g] The low removal efficiency is due to the use of a small amount of plate catalyst in an existing duct.
[h] Design value.

1.7.3 Chubu Electric's Chita Power Station

Chita Station, which is the third largest power station in Japan, has a total capacity of 3300 MW and is the most advanced in NO_x control. Data on its boilers and denitrification processes are given in Table 1-15.

TABLE 1-15. BOILER AND NO_x ABATEMENT DATA FROM CHITA STATION

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Boiler	375	375	500	700	700	700
Capacity (MW)	375	375	500	700	700	700
Boiler Maker	MHI[a]	MHI	MHI	MHI	BH[b]	BH[b]
Operation Start	1965	1966	1967	1974	1978	1978
Fuel	HO[c]	CO[d]	HO	CO	LNG	LNG
NO_x (ppm)	90-100	110-140	90-100	95-100	35-50	35-50
Denitrification Plant						
Process	-	SNR	-	SCR	SCR	SCR
Constructor	-	MHI	-	MHI	Hitachi	Hitachi
Completion	-	1977	-	1980	1978	1978
NO_x After Denitrification (ppm)	-	60-80	-	20	7-10	7-10
NH_3 Emitted (ppm)	-	20-30	-	Below 10	Below 5	Below 5

[a] Mitsubishi Heavy Industries

[b] Babcock-Hitachi

[c] Heavy oil

[d] Crude oil

Under an agreement with local authorities (Chita City and Aichi Prefecture), Chubu Electric keeps NO_x in flue gas from oil-fired boilers below 100 ppm at Chita Station. The combustion modification technologies used include staged combustion, flue gas recirculation, low oxygen combustion, low NO_x burners, and fuel switching to low nitrogen oil containing about 0.1 percent or less N. The flue gas NO_x concentration before the combustion modification was about 400 ppm. Therefore, about 75 percent reduction has been achieved by the modification.

The No. 5 and No. 6 LNG-fired boilers went into operation in 1978. In order to obtain permission from local authorities for the construction of the two new boilers, Chubu Electric had promised to use LNG for fuel and to install SCR units to minimize NO_x emission. In addition, Chubu Electric had promised to install an SCR unit for the No. 4 oil-fired boiler.

Flue gas from the new LNG-fired boilers contains only 35-50 ppm of NO_x, which is treated by SCR to reduce NO_x below 10 ppm. The ammonia content of the flue gas leaving the reactor is kept below 5 ppm. The SCR units were constructed by Hitachi Ltd. Recently construction of the SCR unit for the No. 4 boiler was started to reduce NO_x from 100 ppm to 20 ppm by the MHI process. Ammonia concentration at the reactor outlet will be kept below 10 ppm.

In addition, SNR has been applied to the flue gas from the No. 2 boiler to reduce NO_x from 110-140 ppm to 60-80 ppm (40-45 percent removal) with 20-30 ppm of ammonia in the treated gas.

Chubu Electric plans to install several new oil-fired boilers in other power stations. All of the new boilers will have an SCR plant to remove 80 percent of NO_x.

1.7.4 Efforts by the Steel Industry[4]

Most of the NO_x from the steel industry is derived from iron-ore sintering machines, which use coke, while the rest comes from boilers, coke ovens, heating furnaces and so on.

In 1973, the Japan Steel Federation established a fund amounting to 3 billion yen ($15 million) for promoting studies on NO_x, including its formation mechanism, changes in the atmosphere, health effects, and abatement technologies by combustion modification, flue gas denitrification, and nitrogen removal from coke. Out of the fund, grants have been given to universities for basic studies and to process developers for constructing and operating pilot plants. In addition, the Federation has organized an NO_x study team for its own study of NO_x abatement with a fund of 3.6 billion yen ($18 million).

In 1976 and early 1977, Kawasaki Steel completed two commercial SCR plants at the Chiba Works; this was done in accordance with an agreement reached with Chiba Prefecture and Chiba City for pollution control under the most stringent regulations. Kawasaki Steel signed the agreement because it was constructing a new large blast furnace, and the agreement was needed to start the operation of the blast furnace.

The first commercial SCR plant was constructed to treat 500,000 Nm^3/hr of gas from coke ovens owned by Kawatetsu Chemical, a subsidiary of Kawasaki. The second plant is for treating 750,000 Nm^3/hr of flue gas from iron ore sintering; the gas contains a considerable amount of particulates and SO_3 and is much more difficult to treat than coke oven gas. Gas from sintering is first treated by wet FGD process and then by a wet electrostatic precipitator for further cleaning. Next it is heated to 400°C for SCR by passing through a heater, heat exchanger, and another heater. Although the plant has been operated with few problems, the investment and operation costs are so high that such a process cannot be used widely.

In their search for better ways of NO_x abatement, recipients of the Federation's fund and the NO_x study team have made extensive tests on flue gas denitrification and also on nitrogen removal from coke.

1.7.5 Nitrogen Removal from Coke[4]

Most of the NO_x in flue gas from iron ore sintering is derived from coke, which usually contains about 1 percent nitrogen. Tests have been carried out to reduce the nitrogen content by electrically heating coke up to 1700°C. Following batch tests, a continuous test plant with a capacity of treating 20 tons/day of coke was completed in August 1975 at the Kashima Works, Sumitomo Metal. It has been operated since then in cooperation with Sumitomo Heavy Industries.

A flowsheet of the NR process is shown in Figure 1-14. Pulverized coke is preheated in a two-stage fluidized bed heater and then introduced into an electrical furnace where it is heated up to 1700°C by the electric current through the coke itself. The heated coke is then cooled in a fluidized bed cooler by a circulating gas and new makeup nitrogen. The hot gas discharged from the cooler is sent to the preheaters through cyclones. The gas leaving the preheater is cooled and partly recycled to the fluidized bed cooler, while the rest is sent to a stack through a baghouse.

The relation between the heating temperature achieved and N content of the treated coke is shown in Figure 1-15. About 70 percent of the N in the coke is removed by heating to 1700°C. By removing 70 percent of the N, the NO_x in the flue gas is also reduced by about 70 percent, as illustrated in Figure 1-16; this indicates that most of the NO_x is produced from the nitrogen in the coke.

The pilot plant was completed in August 1975 and put into operation in September. The largest problem has been the degradation of refractories by local overheating and reaction with coke ash. Tests to solve the problem have been carried out in a smaller test furnace with a capacity of 2 t/day.

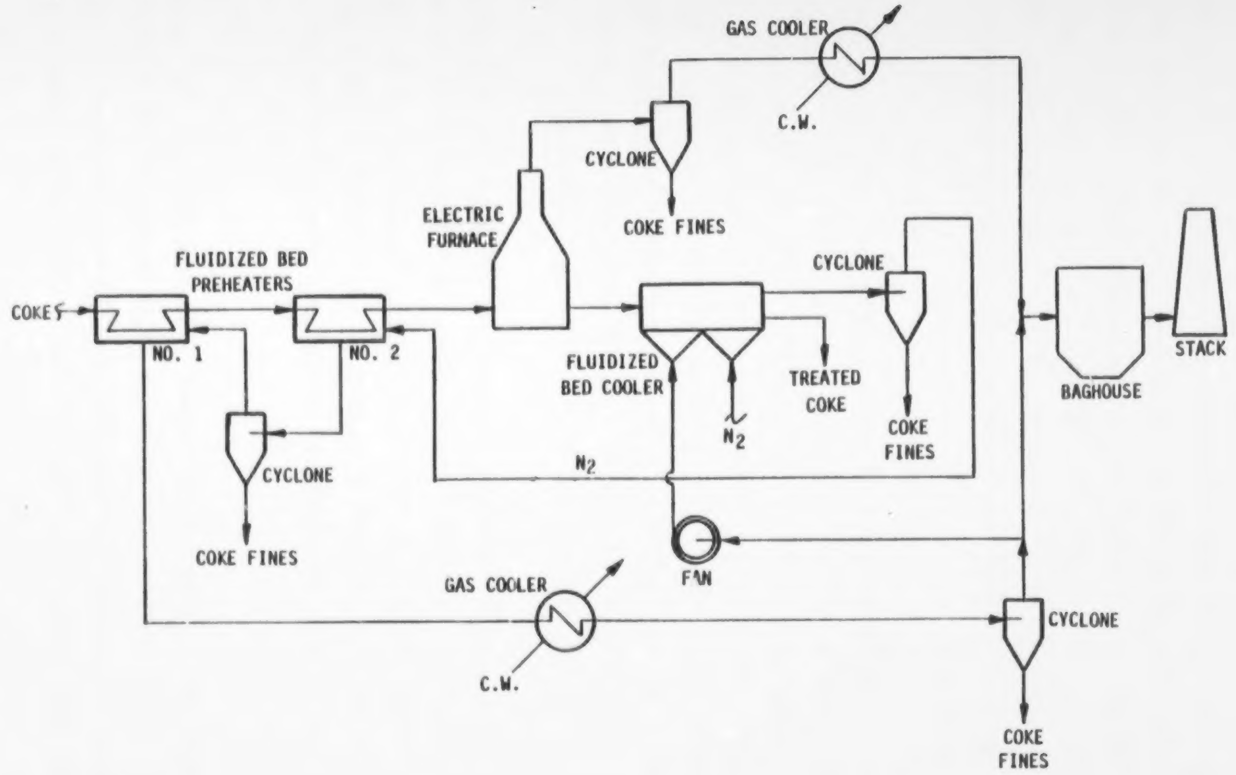
GAS COOLER
C.W.
CYCLONE
COKE FINES
ELECTRIC FURNACE
FLUIDIZED BED PREHEATERS
COKE
NO. 1
NO. 2
CYCLONE
COKE FINES
CYCLONE
FLUIDIZED BED COOLER
N_2
TREATED COKE
COKE FINES
N_2
BAGHOUSE
STACK
FAN
GAS COOLER
C.W.
CYCLONE
COKE FINES

Figure 1-14. Flowsheet of NR process (20 t/day).

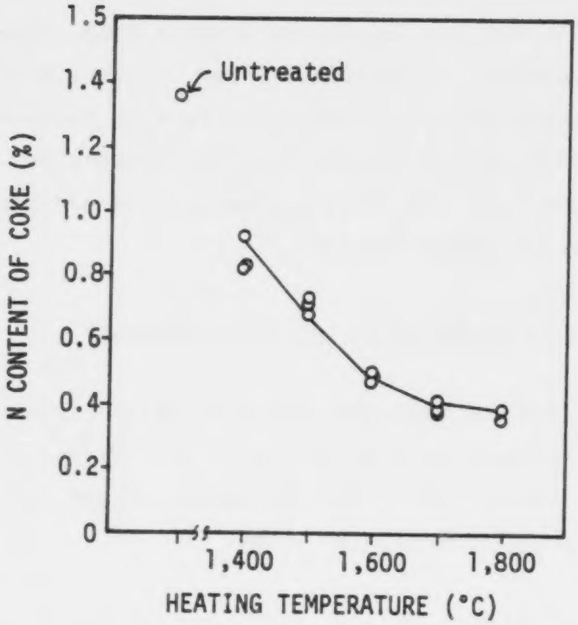

Figure 1-15. Decrease of N in coke by heating (retention time is 2 hours).

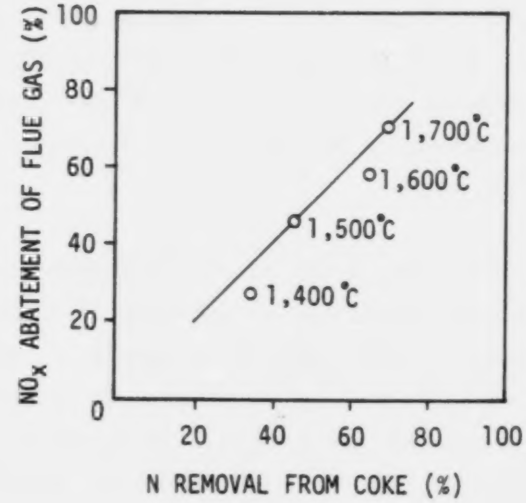

Figure 1-16. NO$_x$ abatement of flue gas from sintering machine by N removal from coke.

It is estimated that the process requires a large amount of electric power, which is equivalent to 30 kWhr per ton of the sintered iron ore, even when smooth operation is achieved. It is also necessary to analyze the composition of the gas discharged from the furnace and to establish a way for its treatment. At the present stage, it is not certain whether or not the process can be commercialized.

1.7.6 Flue Gas Denitrification by the Steel Industry[4]

Gas from the iron ore sintering machine, which has a temperature of about 150°C, usually contains 150-300 ppm of NO_x (virtually all as NO), 150-400 ppm of SO_x (mostly SO_2), 200-300 mg/Nm^3 of particulates containing ferric oxide, and potassium chloride vapor.

The gas is not very suitable for most denitrification processes. For SCR, the gas has to be heated by a heat exchanger and a heater from 150°C to 300-400°C. Moreover, the particulates and potassium chloride vapor tend to contaminate the catalyst. Noncatalytic ammonia reduction is not applicable because of the much higher temperature requirement of 950-1000°C. For wet processes providing simultaneous removal of NO_x and SO_x, the SO_2/NO_x mole ratio is too small to reduce NO_x by the effect of SO_2 as a reducing agent. Among the NO_x removal processes, SCR at a low temperature of 250-300°C and simultaneous removal of SO_x and NO_x by activated carbon at 200-250°C seem relatively suitable.

With the Federation's fund, 4 SCR pilot plants were constructed and operated using the processes developed by JGC Corp. (parallel passage reactor), Mitsubishi Kakoki Kaisha (MKK; Sarc catalyst), Sumitomo Heavy Industries (activated carbon), and Kurabo-Niigata Iron (moving bed reactor). The pilot plants are located in steel works. They have a capacity of treating 1000-2000 Nm^3/hr of flue gas from iron-ore sintering machines or coke ovens. In addition, many pilot plants have been operated by the NO_x study team and also by each steel producer (Table 1-16).

TABLE 1-16. DENITRIFICATION PLANTS OF STEEL INDUSTRY

Plant Owner	Plant Site	Process	Process Developer	Gas Treated		Completion
				Nm^3/hr	Source	
Kawasaki Steel	Chiba	SCR	Hitachi Zosen	5,000	SM[b]	1974
Kawasaki Steel	Mizushima	SCR	Mitsubishi Kakoki	1,500	SM	1975
Kawatetsu Chemical[a]	Chiba	SCR	Hitachi Ltd.	500,000	CO[c]	1976
Kawasaki Steel	Chiba	SCR	Hitachi Zosen	750,000	SM	1977
Nippon Steel	Yawata	SCR	Nippon Steel	1,600	SM	1976
Nippon Steel	Kagoya	SCR	JGC	2,000	SM	1976
Nippon Steel	Yawata	EB[d]	Ebara	3,000	SM	1977
Nippon Steel	Kimitsu	SCR	JGC	150,000	CO	1978
Nippon Kokan	Keihin	SCR	Nippon Kokan	15,000	SM	1976
Sumitomo Metal	Amagasaki	Wet(Na)	Sumitomo-Fujikasui	62,000	Boiler	1973
Sumitomo Metal	Kashima	Wet(Ca)	Sumitomo-Fujikasui	25,000	SM	1976
Sumitomo Metal	Wakayama	Carbon	Sumitomo H.I.	2,000	SM	1975
Kobe Steel	Kakogawa	Wet	Kobe Steel	10,000	SM	1976
Kobe Steel	Kakogawa	SCR	Kobe Steel	1,000	SM	1976
Kobe Steel	Kakogawa	SCR	Kobe Steel	1,000	CO	1976
Nakayama Steel	Funamachi	SCR	Kurabo-Niigata	2,000	CO	1975

[a] Subsidiary of Kawasaki Steel.
[b] Sintering machine.
[c] Coke oven.
[d] Electron beam radiation.

1.7.7 NO_x Abatement by Other Industries

The oil, petrochemical, and chemical industries have installed about 30 commercial SCR plants (Table 3-1) and 5 SNR plants (Table 5-1) for the denitrification of flue gases from boilers and heating furnaces.

The ceramic industry has also emitted a considerable amount of NO_x. Cement kilns and glass furnaces are two major sources of NO_x from the industry. A rotary kiln for cement calcination has a wide range of hot zones and gives off 400-800 ppm of NO_x even when fired with oil. Pilot plant tests have been carried out by the Cement Industry Association in an attempt to reduce NO_x emissions by flue gas denitrification using SCR, but the tests were not successful because the gas has a high particulate loading and contains an appreciable amount of alkaline compounds which affects the catalyst. A new type of cement kiln will be installed in new plants. The new type kiln has a suspension preheater for which more than half of the fuel is used; this results in a considerable reduction of the hot zone area. The NO_x concentration in the flue gas is reduced to about 150 ppm.

Flue gas from a glass furnace contains a considerable amount of sodium sulfate vapor, which deposits on the SCR catalyst and lowers its activity. Either the alkaline vapor has to be removed in advance, or the catalyst has to be washed to remove the sulfate. Tests to reduce NO_x to N_2 by reducing gases without a catalyst have also been carried out. Nonetheless, flue gas denitrification continues to be a problem for the gas from glass furnaces.

Tail gas from nitric acid plants contains 500-2000 ppm of NO_x. Sodium scrubbing to produce sodium nitrite as a by-product, catalytic reduction to convert NO_x to N_2, and absorption using zeolite (molecular sieve) have been commercially applied. Treatment of the tail gas is not difficult because the gas is clean, containing no SO_x and particulates.

1.8 REFERENCES

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2. Environment Agency. Recent Countermeasures for Air Pollution Control in Japan. (After OECD Review of Japanese Environmental Politics in 1976.) Japan, 1977. (In English.)

3. MITI, Industrial Pollution Control Association. Countermeasure of NO_x Pollution. Japan, December 1977.

4. Japan Steel Federation. Present Status of Development of NO_x Abatement Technology by the Steel Industry. April 1977.

SECTION 2

NO_x ABATEMENT BY COMBUSTION MODIFICATION (CM)

2.1 CLASSIFICATION OF COMBUSTION MODIFICATION TECHNIQUES

NO_x emissions from combustion processes are formed by two mechanisms: the oxidation of nitrogen in air at high temperatures, and the combustion of various nitrogen compounds contained in fuel. The former is called "thermal NO_x," and the latter "fuel NO_x."

Formation of thermal NO_x can be reduced effectively by combustion modifications, such as decreasing the oxygen concentration in the combustion regions; shortening the residence time of combustion gases in high temperature zones; or lowering the flame temperature. Reduction of fuel NO_x emissions is achieved by decreasing the oxygen concentration in the combustion reaction zone and switching to a low-nitrogen fuel.

Combustion modification techniques used widely in Japan for NO_x control can be classified into four categories:

- Change of operating conditions
    1) Low-excess-air combustion
    2) Change in contacting of fuel with air in combustion chamber
    3) Reduction of heat load in combustion chamber (reduction of output power)
    4) Lowering of air preheating temperature

- Modification of burner design

- Modification of combustion system design
    1) Reduction of heat load in combustion chamber (increase of furnace volume)
    2) Staged combustion
    3) Flue gas recirculation
    4) Water or steam injection

- Other methods
    1) Change of fuel
    2) Modification of firing

Combinations of the above techniques are also in practical use. Although operating conditions can be changed relatively easily in existing installations, the changes usually reduce the NO_x emissions only slightly and often cause operating difficulties. On the other hand, modifications of the burner and combustion system design are promising control techniques. Fewer problems are encountered when design modifications are incorporated in new plants; relatively large reconstruction costs are required when the modifications are applied to existing installations.

The principles and characteristics of NO_x control techniques are described in the following section.

2.2 CHANGE OF OPERATING CONDITIONS

2.2.1 Low-Excess-Air Combustion (LEA)

Low-excess-air combustion, a means of preventing low-temperature corrosion caused by SO_3 in large boilers, is also useful in NO_x abatement. LEA combustion reduces the formation of thermal NO_x and fuel NO_x by decreasing the oxygen concentration in combustion regions. There it has been applied to large boilers burning high-nitrogen fuels, such as grade B (0.08-0.35 percent N) or grade C (0.20-0.35 percent N) heavy oil. On the other hand, the technique is not widely used with small boilers. The reasons are:

- Small boilers usually burn low-nitrogen fuels such as kerosene, grade A heavy oil (0.005-0.08 percent N), or gas. Thus, there is no need to attempt fuel NO_x reduction.
- Small boilers normally are unmanned, and their operation is not very well controlled. Therefore, operation with low excess air in these boilers tends to cause incomplete combustion.

Recently, LEA combustion has been applied to large metal heating furnaces as a means of NO_x abatement and fuel conservation.[1]

2.2.2 Improvement of Fuel/Air Mixing Conditions in Combustion Chamber

It has been reported that NO_x is reduced considerably through a slight adjustment of the air register, for example, a change in the vane angle. The reduction may be due to the change in mixing condition in the combustion chamber. Few existing installations use this technique.

Reduction of NO_x by a change in mixing conditions is achieved either with very good or poor mixing. With good mixing, the combustion rate increases and temperature in the reaction zone becomes high. Yet thermal NO_x formation can be reduced because the residence time in the high temperature region can be shortened. When the mixing condition is poor, the combustion rate slows down and the flame temperature drops. This results in the reduction of both thermal and fuel NO_x emissions in the same way as in the staged-combustion type burner. (The latter is discussed in section 2.3.5.)

Changing the air system makes it necessary to readjust the air/fuel ratio. An improper adjustment may increase the formation of unburned products such as soot, carbon monoxide, and hydrocarbons, or may cause unstable combustion.

2.2.3 Reduction of Heat Release Rate in the Combustion Chamber (Reduction of Output Power)

Generally, when the heat load in the combustion chamber decreases, the flame temperature is lowered and thermal NO_x emissions are reduced. The use of this method in existing installations, however, results in a decrease in fuel efficiency and output power. Therefore, this method is regarded only as an emergency measure.

2.2.4 Reduction of Air Preheating

Lowering of the air preheating temperature reduces the flame temperature and consequently the formation of thermal NO_x. This method is seldom used in existing installations because it also reduces fuel efficiency. Moreover, its application is limited to large boilers with air preheaters, for which better control techniques are available.

2.3 MODIFICATION OF BURNER DESIGN

2.3.1 Introduction

This method reduces NO_x with the use of an improved burner, the so-called low-NO_x burner (LNB). Low-NO_x burners developed in Japan are mostly applied to boilers and various kinds of furnaces. They may be classified into five types:

- Good-mixing
- Divided-flame

- Self-recirculation
- Staged-combustion
- Combination

Large low-NO_x burners developed so far have capacities of 5×10^7 kcal/hr for boilers and 2×10^7 kcal/hr for heating furnaces which are large enough for commercial use.

2.3.2 Atomizing Type Burners

Atomizing type low-NO_x burners are useful in reducing the formation of thermal NO_x by shortening the residence time of combustion gas in high temperature regions. They have little effect on reducing fuel NO_x, however, because of the high oxygen concentration in the initial stage of combustion.

An example of an atomizing type low-NO_x burner is illustrated in Figure 2-1. This burner, developed by Nippon Furnace Kogyo Kaisha Ltd., is called the NFK-TRW burner because it has been commercialized under a technical license agreement with Civiltech Corp. (U.S.) in a joint venture with TRW Inc.

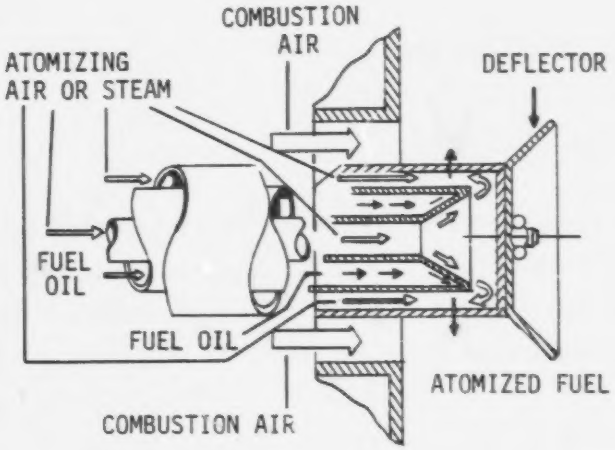
COMBUSTION AIR
ATOMIZING AIR OR STEAM
DEFLECTOR
FUEL OIL
FUEL OIL
ATOMIZED FUEL
COMBUSTION AIR

Figure 2-1. NFK-TRW Burner.

In this burner, atomizing of fuel with air is achieved by impinging the air stream at nearly right angles against the jets of fuel injected radially outward through a large number of shaped ports. The air and fuel are then further mixed by means of a deflector, which functions as a flame holder. The mixture of fuel and air produces a thin, conical flame according to the flow pattern. Due to the concical shape, a maximum radiation surface is produced, and heat from the flame is rapidly removed. Therefore, the residence time of combustion gas in the high temperature regions is shortened, and thermal NO_x is reduced. The NO_x concentrations produced using the burner at various operating conditions are shown in Figure 2-2. Burners which can burn either oil or gas have been commercialized. They reduce not only NO_x, but also soot emissions. In addition, they allow the heat load in the combustion chamber to be maintained as high as before, thereby increasing fuel efficiency. These burners are applicable only to boilers, however, because of their flame shape. The pressure drop at the burner throat is relatively high.

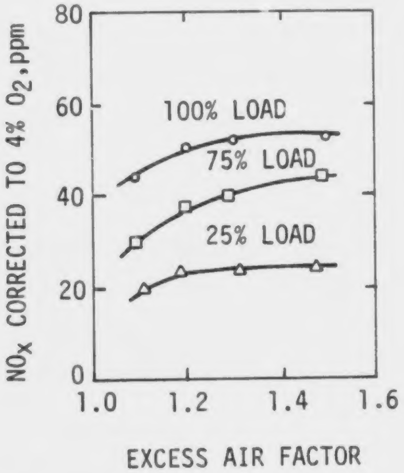

Figure 2-2. Effect of NFK-TRW Burner on NO_x. (Fuel, grade A fuel oil; air temperature, 25°C; maximum fuel flow rate, 380 ℓ/hr)

2.3.3 Divided-Flame Type Burners

In the divided-flame type low-NO_x burner for heavy oil, the flame is divided into several independent small flames by means of grooved nozzle tips. This prevents mutual interference between small flames. Hence, the flame temperature and the residence time in the high temperature regions decrease, resulting in thermal NO_x reduction.

The burner, developed by Ishikawajima-Harima Heavy Industries Ltd. (IHI), is shown in Figure 2-3. Its effect when combined with other NO_x control techniques is illustrated in Figure 2-4.[3] The two curves indicate the practical upper limit and lower limit. NO_x reduction with this burner decreases with an increase in the effects of other control techniques. For example, the reduction ratio due to the effect of the burner ranges from 18-42 percent without other CM techniques and from about 10-30 percent when 40 percent reduction is achieved by other techniques.

2.3.4 Self-Recirculation Type Burners

The configuration of the self-recirculation type burner is shown in Figure 2-5. This burner has been developed by Daido Tokushuko Co. under a technical license agreement with Caloric Gesellschaft für Apparate Bau (West Germany).[4]

It reduces both thermal and fuel NO_x formation in such a manner that partially combusted hot gas is reintroduced into the initial stage of combustion by the fuel jet and atomizing air or steam. Thus, both vaporization of fuel and firing in the low-oxygen-concentration zone are accomplished in the initial stage of combustion.

This burner's effect on NO_x reduction is illustrated in Figure 2-6. This type of burner is effective not only for NO_x reduction, but also for soot suppression by hot combustion gas recirculation. It is used in metal heating furnaces that burn oil and gas.

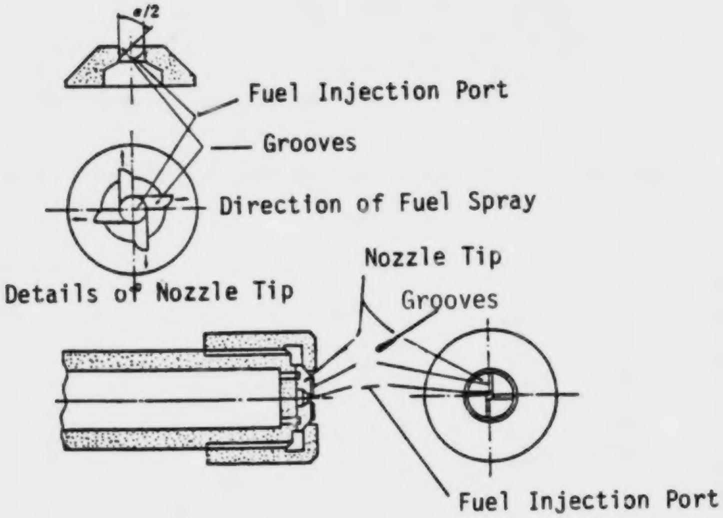
θ/2
Fuel Injection Port
Grooves
Direction of Fuel Spray
Nozzle Tip
Details of Nozzle Tip
Grooves
Fuel Injection Port

Figure 2-3. Divided-flame type burner.

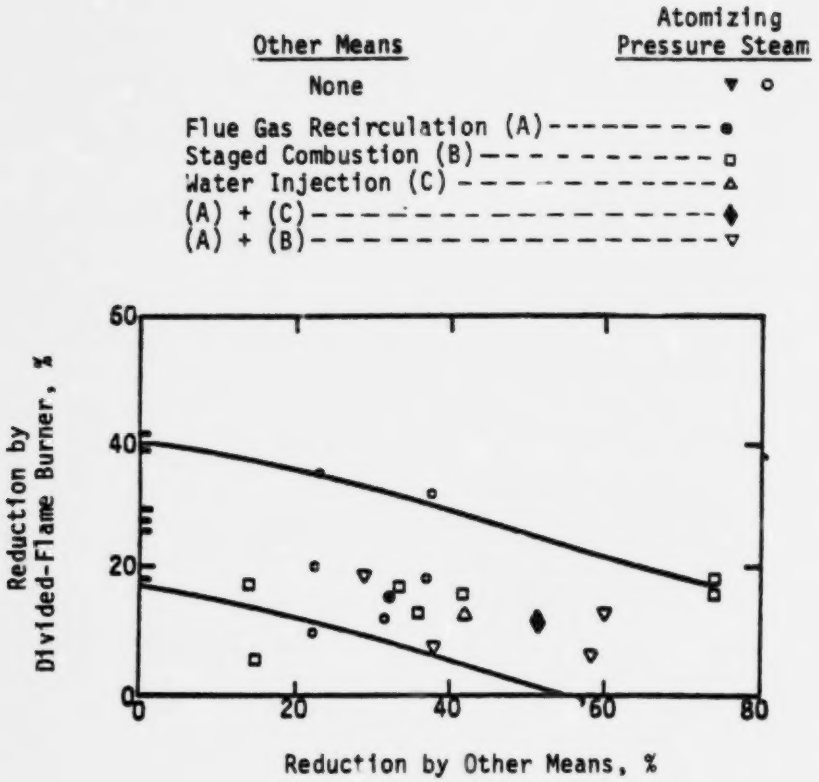

Figure 2-4. NO_x reduction by divided-flame type burner and other means.

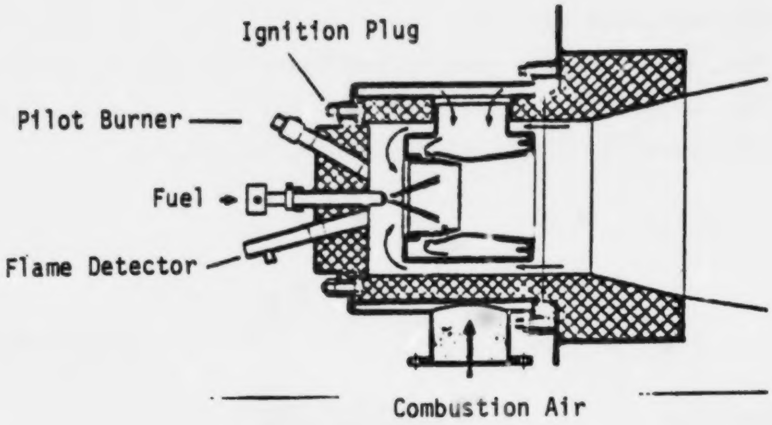
Ignition Plug
Pilot Burner
Fuel
Flame Detector
Combustion Air

Figure 2-5. Self-recirculation type burner.

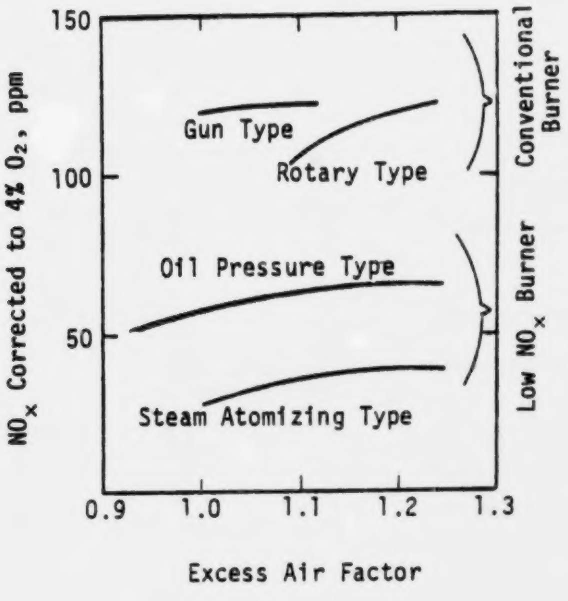

Figure 2-6. Effect of self-recirculation type burner on NO$_x$ reduction. (Fuel, grade A oil; Fuel flow rate, 100 ℓ/hr)

A burner designed exclusively for gas firing is shown in Figure 2-7. This burner developed by Sanray Reinetsu Co., Ltd., is called the XB burner. Several fuel gas injection nozzles are installed circularly to shorten the flame. NO_x levels are presented in Figure 2-8. A similar type of burner has been developed by Chugai Ro Kogyo Co., Ltd.

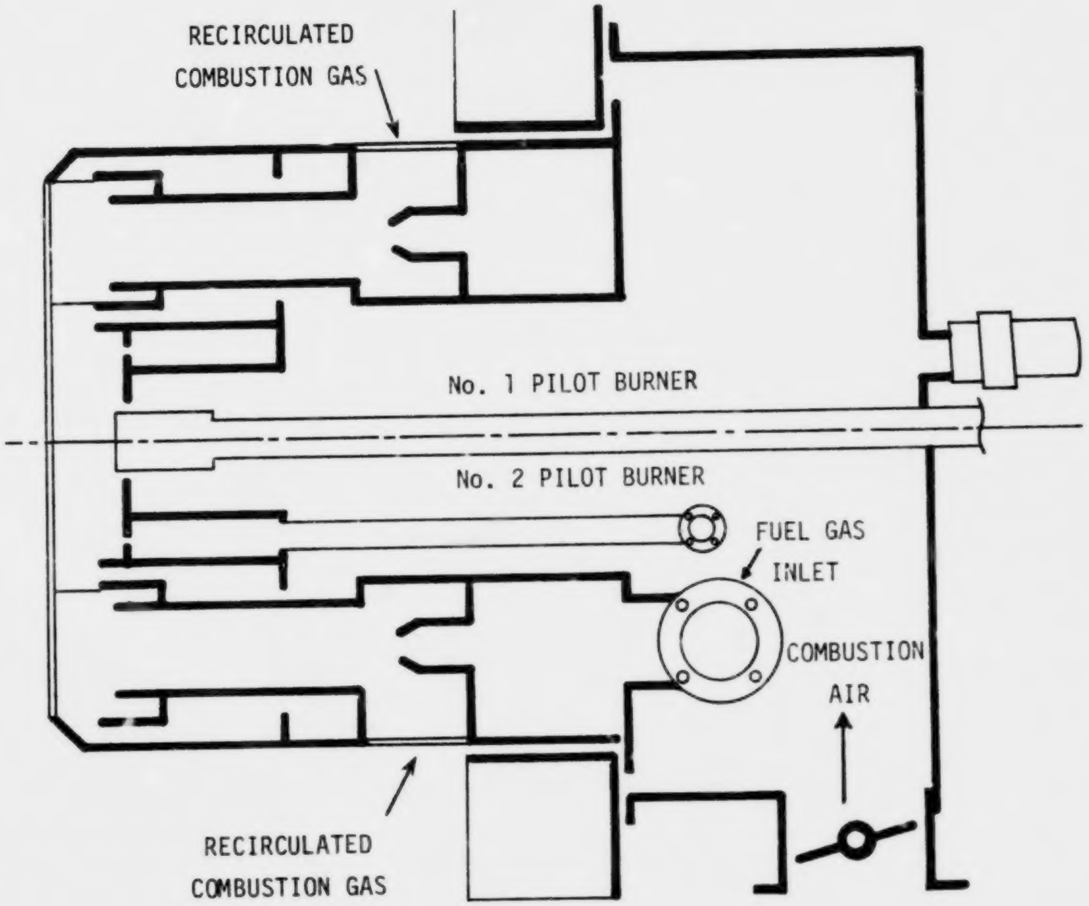
RECIRCULATED
COMBUSTION GAS
No. 1 PILOT BURNER
No. 2 PILOT BURNER
FUEL GAS
INLET
COMBUSTION
AIR
RECIRCULATED
COMBUSTION GAS

Figure 2-7. XB Burner.

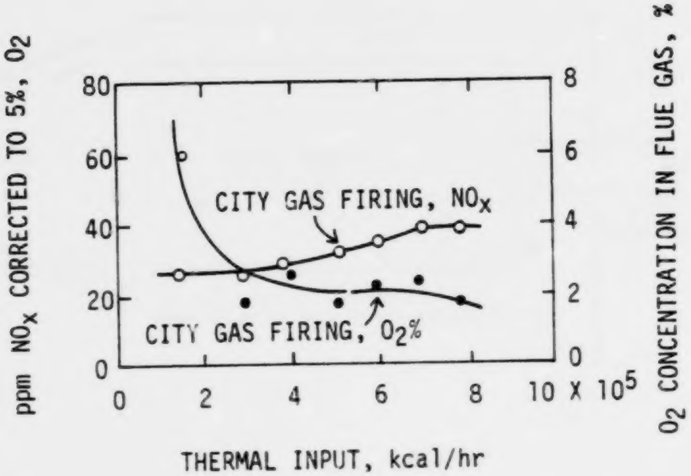

Figure 2-8. Effect of XB burner on NO_x emission levels.

2.3.5 Staged-Combustion Type Burners

Staged-combustion type burners are divided roughly into a two-stage combustion group and an off-stoichiometric combustion group. Burners in the two-stage combustion group are classified according to the equivalence ratio in the first stage into fuel-rich and air-rich. The fuel-rich type is used usually for two-stage combustion, and the air is added in the second stage; fuel-rich type burners are shown in Figures 2-9, 2-11, and 2-13. In the air-rich type, fuel is injected in the second stage; an example of this type of burner is presented in Figure 2-15.

Figure 2-9 illustrates the APOC burner developed by Tokyo Gas Company for firing town gas.[5] A more advanced burner of this type has a catalyst at the outlet of the preliminary combustion region for further reduction of NO_x. Figure 2-10 shows the emission levels with this burner. HCN and NH_3 are likely to play a significant role in NO_x formation in the second stage. The catalyst decreases this problem by reducing HCN and NH_3 together with NO_x in the first stage. The advanced type is not yet used commercially.

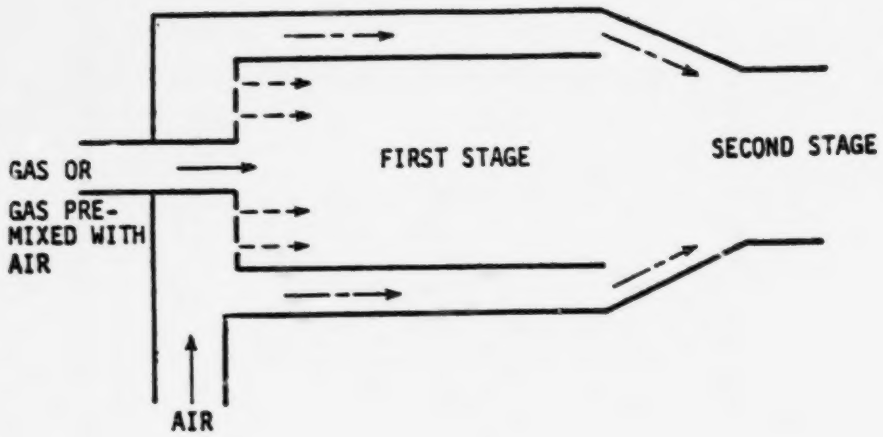
FIRST STAGE
SECOND STAGE
GAS OR
GAS PRE-
MIXED WITH
AIR
AIR

Figure 2-9. APOC burner.

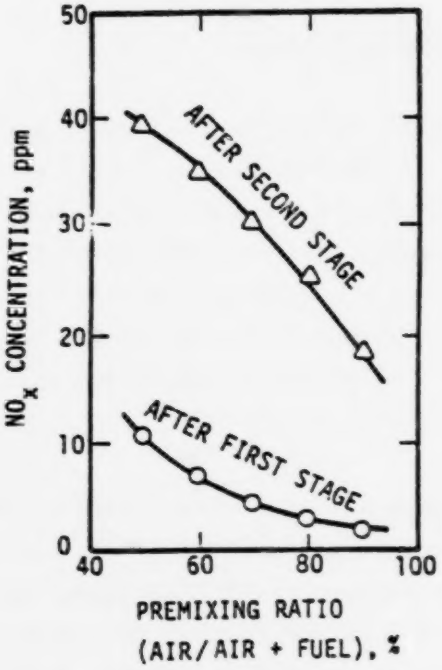

Figure 2-10. NO_x emission levels from a low-NO_x burner more advanced than the one shown in Figure 2-9. (Fuel, methane; thermal input, 95,000 kcal/hr; NO_x concentration corrected to 0 percent O_2)

The FH burner illustrated in Figure 2-11, used for LPG, heavy oil or kerosene fuels, is also of the fuel-rich type.[6] Figure 2-12 shows its effect on NO_x reduction. This burner, developed by Chugai Ro Kogyo Co., Ltd., is used in the heating furnace. Similar types of burners have been developed by many manufacturers because of their relatively simple configuration and the capability of fuel NO_x reduction. These manufacturers include Mitsubishi Heavy Industries, Ltd., Kawasaki Heavy Industries, Ltd., Osaka Gas Company, Sanray Reinetsu Co., Ltd. and Rozai Kogyo Co., Ltd.

The fuel-rich type burner shown in Figure 2-13 was designed for use with pulverized coal by Babcock Hitachi Co., Ltd.; it is called the dual-air register type burner and is used in utility boilers. This burner is effective for NO_x reduction, as shown in Figure 2-14. IHI has developed a similar type of burner.

An air-rich type two-stage combustion burner is shown in Figure 2-15.[8] This burner, developed by Tokyo Gas Company for gas firing, is called the TGS burner. The effect of the TGS burner on NO_x reduction is illustrated in Figure 2-16. In the first stage, the flame temperature is decreased due to high-excess-air combustion; in the second stage, the oxygen concentration is lowered due to low-excess-air combustion. These decreases in flame temperature and oxygen concentration provide NO_x reduction. It is unlikely, however, that complete combustion can be accomplished for oil or coal firing.

The basic structure of the off-stoichiometric combustion (OSC) type burner for oil firing is presented in Figure 2-17.[9] This burner has been developed by MHI for boilers using grade A heavy oil or kerosene. The fuel sprayed in the upper and lower compartments is evaporated by preheated air and premixed with air resulting in combustion. In the middle compartment, a normal diffusion flame is produced. Thus, off-stoichiometric combustion is realized. To reduce NO_x further, recirculated flue gas is mixed with air. MHI guarantees less than 70 ppm of NO_x with this system (see Figure 2-18).

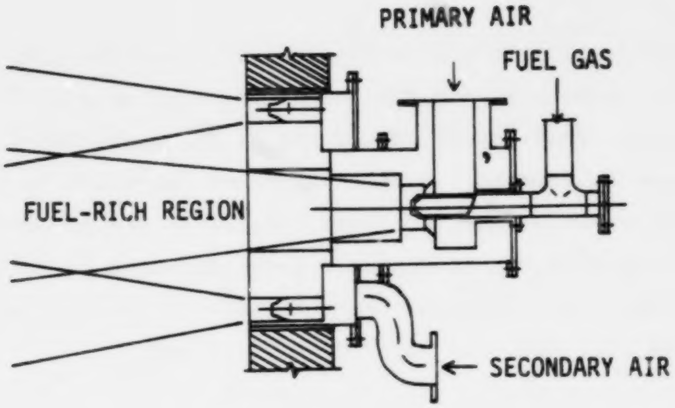
PRIMARY AIR
FUEL GAS
FUEL-RICH REGION
SECONDARY AIR

Figure 2-11. Schematic of FH burner.

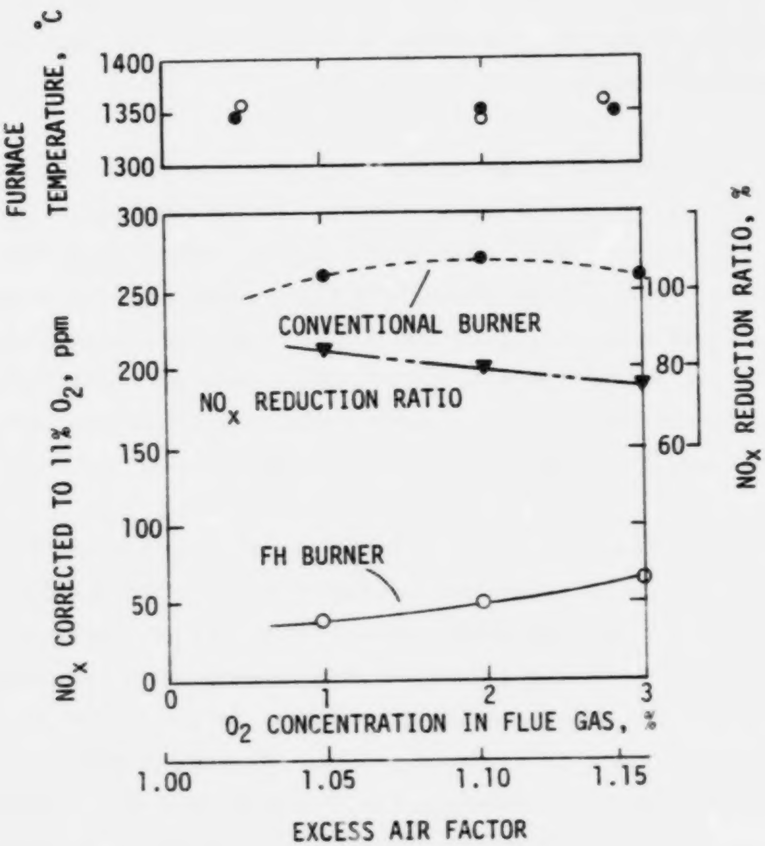

Figure 2-12. FH burner's effect on NO_x reduction.

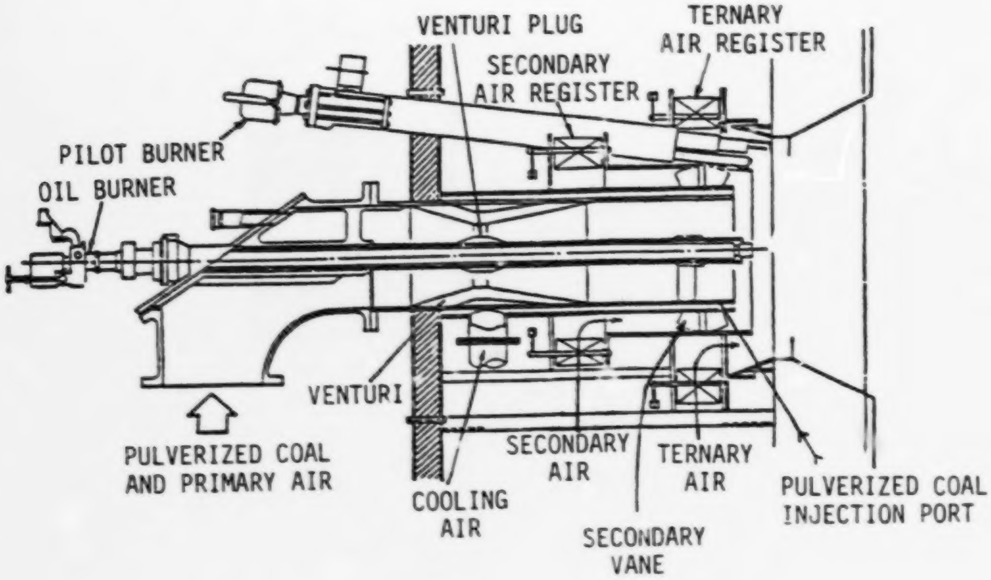
VENTURI PLUG
TERNARY AIR REGISTER
SECONDARY AIR REGISTER
PILOT BURNER
OIL BURNER
VENTURI
PULVERIZED COAL AND PRIMARY AIR
COOLING AIR
SECONDARY AIR
TERNARY AIR
PULVERIZED COAL INJECTION PORT
SECONDARY VANE

Figure 2-13. Dual-air register type burner for use with pulverized coal.

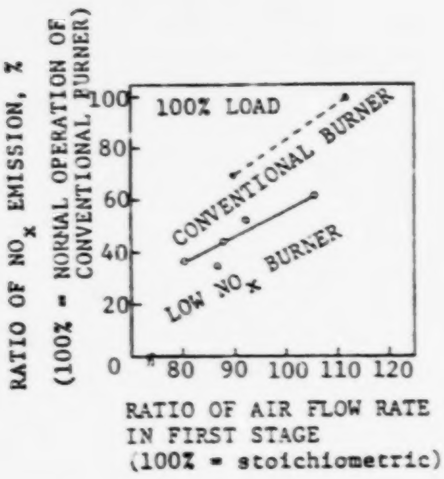

Figure 2-14. Effect of low-NO$_x$ burner shown in Figure 2-13. (Boiler capacity, 810 tons/hr; nitrogen content in fuel, 0.89-1.21 percent)

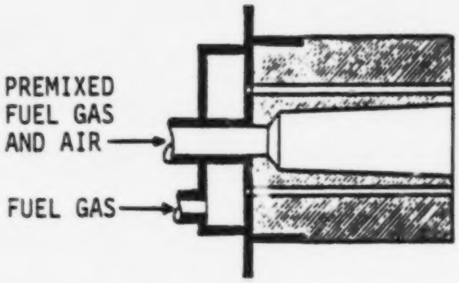
PREMIXED
FUEL GAS
AND AIR
FUEL GAS

Figure 2-15. Schematic of TGS burner.

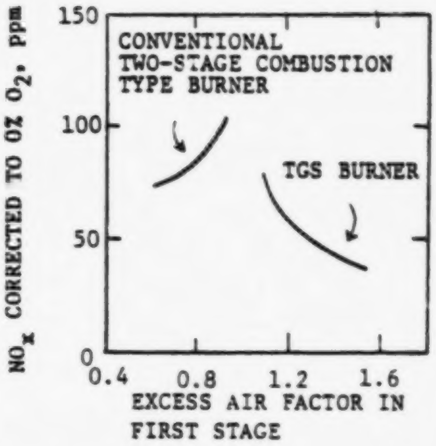

Figure 2-16. Effect of TGS burner on NO_x reduction. (Fuel, methane; thermal input, 2×10^5 kcal/hr; total excess air factor, 1.10; furnace temperature, 1,200°C)

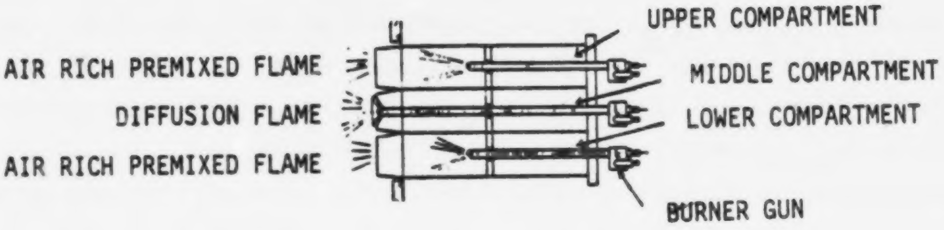
UPPER COMPARTMENT
AIR RICH PREMIXED FLAME
MIDDLE COMPARTMENT
DIFFUSION FLAME
LOWER COMPARTMENT
AIR RICH PREMIXED FLAME
BURNER GUN

Figure 2-17. Basic structure of OSC type burner.

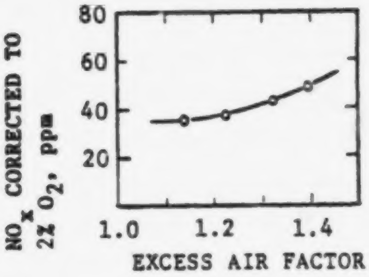

Figure 2-18. NO_x emission levels of the burner shown in Figure 2-17 with propane. (Air temperature, 250°C; thermal input, 3.5 x 10^7 kcal/hr; flue gas recirculation ratio, 15 percent)

Figure 2-19 shows the arrangement of the fuel injection holes of atomizing nozzles in an off-stoichiometric combustion burner for oil firing; this OSC burner was developed by Volcano Company.[10] The main feature of its atomizer is that not all of the fuel-injection holes are of the same size. As combustion air is uniformly admitted around the atomizer, the fuel-injection holes with larger diameters produce fuel-rich combustion zones, whereas the smaller holes produce fuel-lean regions. Therefore, off-stoichiometric combustion is achieved. Since several different arrangements of fuel-injection holes are available, the optimum arrangement may be determined by experimentation. Because of the ease of installation and the low cost, this burner has been used widely. NO_x levels produced by such a burner are presented in Figure 2-20. This burner tends to increase soot emissions when excess air is low, because some of the flame zones are deficient in oxygen. A similar type of burner has been developed by Babcock Hitachi Co., Ltd.

2.3.6 Combination Type Burners

There are several low-NO_x burners which combine the above-mentioned methods. For example, the burner illustrated in Figure 2-21 combines two-stage combustion and self-recirculation of hot combustion gas. It is called the SRG burner, and was developed by Nippon Furnace Kogyo Kaisha, Ltd.[2] This burner is adopted mainly in oil heating furnaces and boilers. The effect of the burner on NO_x reduction is shown in Figure 2-22. Figure 2-23 illustrates a similar type of burner (the TCG) developed by Osaka Gas Company.[11]

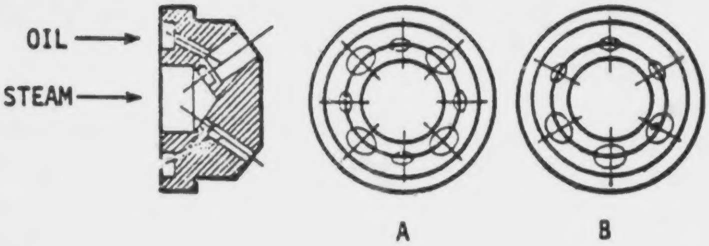

Figure 2-19. Atomizing nozzles in off-stoichiometric combustion-type low-NO_x burner for oil.

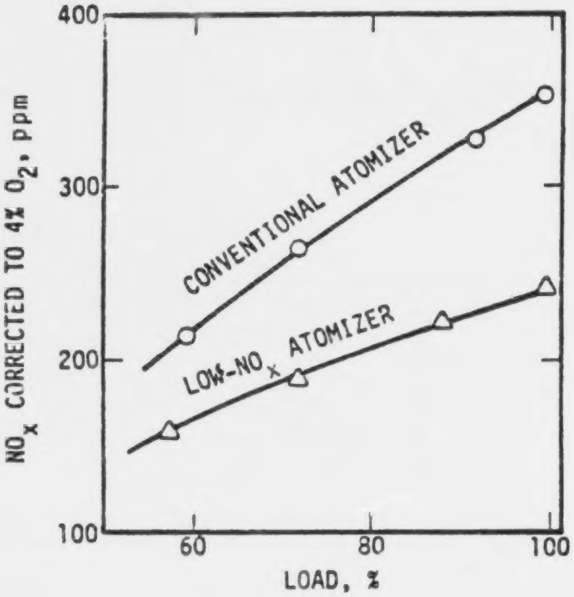

Figure 2-20. Effect of low-NO_x atomizer shown in Figure 2-19 on NO_x emissions. (Boiler capacity, 55 t/hr; fuel, grade C heavy oil; air temperature, 280°C)

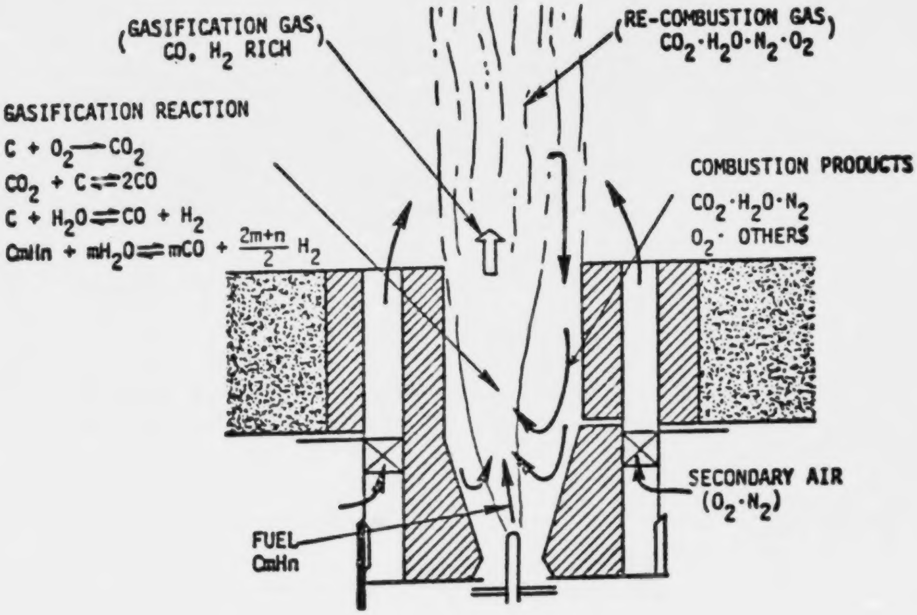
GASIFICATION GAS
CO, H2 RICH
RE-COMBUSTION GAS
CO2·H2O·N2·O2
GASIFICATION REACTION
C + O2 → CO2
CO2 + C ⇌ 2CO
C + H2O ⇌ CO + H2
CmHn + mH2O ⇌ mCO + (2m+n)/2 H2
COMBUSTION PRODUCTS
CO2·H2O·N2
O2· OTHERS
SECONDARY AIR
(O2·N2)
FUEL
CmHn

Figure 2-21. Schematic of SRG burner.

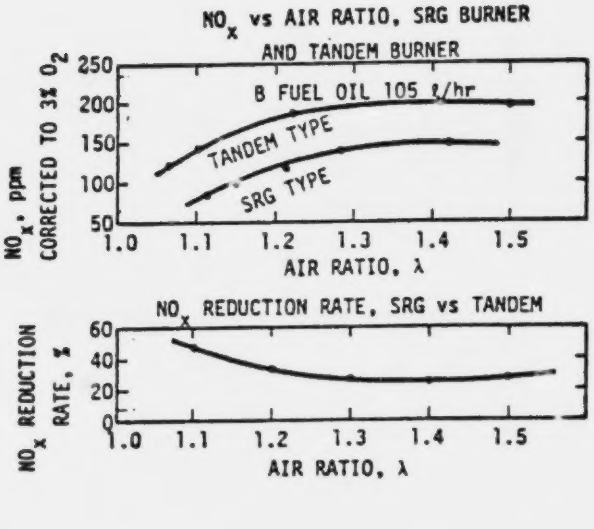

Figure 2-22. Effect of SRG burner on NO_x reduction.

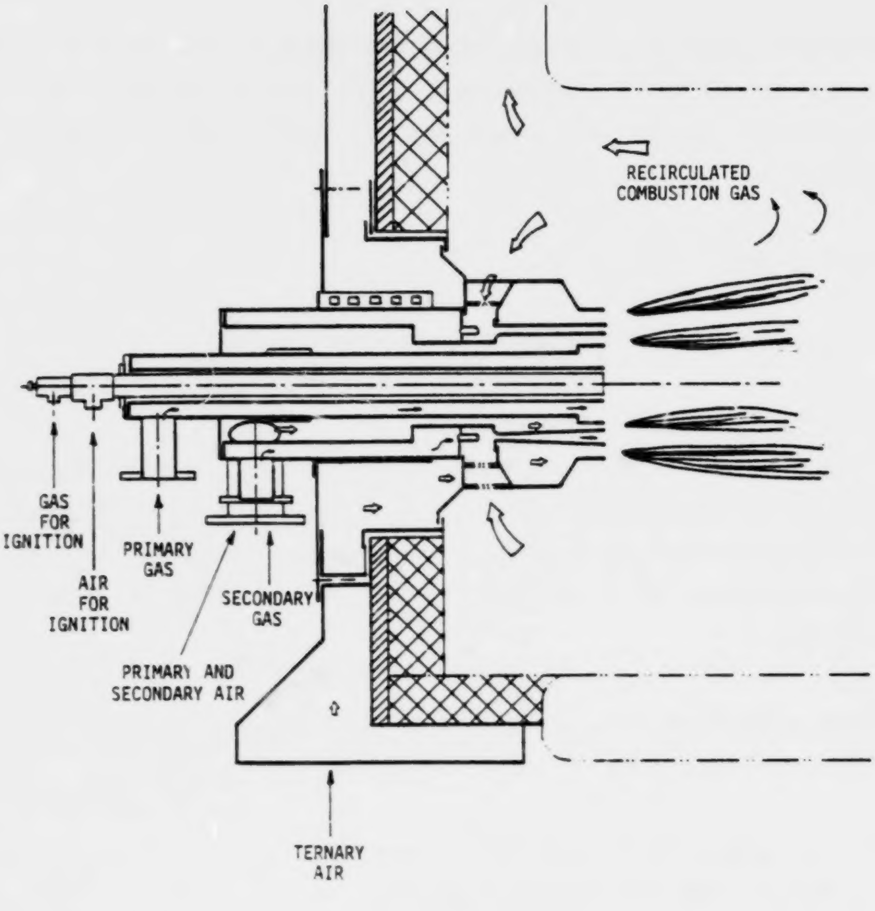
RECIRCULATED COMBUSTION GAS
GAS FOR IGNITION
AIR FOR IGNITION
PRIMARY GAS
SECONDARY GAS
PRIMARY AND SECONDARY AIR
TERNARY AIR

Figure 2-23. TCG burner.

2.4 MODIFICATION OF COMBUSTION SYSTEM DESIGN

2.4.1 Reduction of Heat Release Rate in the Combustion Chamber (Increase of Furnace Volume)

Manufacturers currently are designing boilers and furnaces with heat release rates about 10 to 20 percent lower than those of conventional ones. The new boilers and furnaces are larger and more easily adaptable to NO_x control techniques.

2.4.2 Staged Combustion

There are two major categories of staged combustion:

1) Two stage combustion (TSC)*

In two-stage combustion, about 70 to 90 percent of the stoichiometric air is admitted into the first stage. The additional air is then added downstream to obtain complete combustion. With this technique, both thermal and fuel NO_x are reduced by fuel-rich (low-oxygen concentration) combustion in the first stage.

Two stage combustion is classified into four types, depending on the locations of second-stage air ports:

a) On the furnace wall above the burners.
b) Top burners for air injection only.
c) Side or rear walls of the furnace.
d) On the circumference of the burners.

Large boilers installed in power plants employ type a or b. Type b, called quasi-two-stage combustion, is used in units to which type a cannot be applied. Types c and d are used in medium- and small-capacity boilers.

---

*The number of stages seldom exceeds two.

Type c is not popular for retrofitting water tube boilers because it requires considerable revisions. Type d, which is illustrated in Figure 2-24, can be readily applied to small installations with a single burner because it calls for minor revisions. Two-stage combustion cannot be applied to installations with furnace dimensions that cannot accommodate greater flame lengths. Also two-stage combustion tends to increase the amount of unburned products; thus the unconsumed air increases in the flue as with normal combustion. When the air injection ports in the second stage are suitably located, further NO_x reduction is obtained.[12]

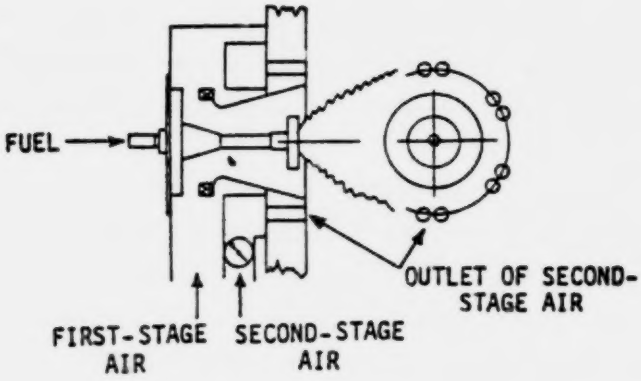

Figure 2-24. Two-stage combustion for small boiler.

2) Off-stoichiometric combustion (OSC)

This method has an effect similar to that of two-stage combustion; it is readily adapted to medium- and small-size boilers with several burners, to which two-stage combustion is not easily applied.

In this technique, the fuel-rich burners and air rich burners or air ports are suitably located. The fuel-rich portions reduce the oxygen concentration, and the air-rich portions decrease the temperature by means of the excess air; thus, NO_x formation is reduced. Combustion in the fuel-rich portions is completed upon mixing due to the excess air in the air-rich portions.

The location of fuel-rich and air-rich burners or air ports is decided after a systematic test. Often, it is effective to place the air-rich burners or air ports in the central upper parts of the furnace walls, or in the regions of highest heat release.

2.4.3 Flue Gas Recirculation (FGR)

In flue gas recirculation, part of the flue gas is mixed with combustion air and sent into the furnace. Thus, NO_x is reduced through the decrease of flame temperature resulting from the increase of the total heat capacity of combustion gas. Thermal NO_x formation can therefore be reduced.

Recirculation ratios are limited to about 30 to 40 percent to prevent unstable firing, although this limit is lower with larger units. Keeping the recirculation ratios in suitable ranges may improve combustion conditions and decrease the soot formation. However, the decrease of flame temperature alters the distribution of heat transfer and lowers the fuel efficiency of existing installations.

A recirculation fan and additional duct work are required to implement flue gas recirculation. As a result, installation cost is considerably higher, and more installation space is required than for the other methods. Therefore, this method is not used with small boilers or furnaces.

2.4.4 Water or Steam Injection

Water or steam injection reduces thermal NO_x emissions mainly by decreasing the flame temperature. There are two injection methods:

1) Injection into the combustion chamber. (This includes increasing the steam flow rate in the atomizer.)

2) Mixing water with the fuel (emulsification).

Injection ports close to the burners are effective for the first method. Thus, burners with water injection ports are adopted. The upper limit of the injection rate is about 5 kg/10^4 kcal.

With the use of this technique, formation of soot decreases, so it is possible to reduce the excess air. Therefore, the decrease in thermal efficiency may not be great.

There are two kinds of emulsified fuel: water droplets dispersed in oil (W/O type) and oil dispersed in water (O/W type). The former type can be used for NO_x reducing fuel because the resulting emulsion viscosity is lower than that of the O/W type reducing the pumping power requirements.

With the use of emulsified fuel oil, the atomized oil droplets are separated into very fine particles by sudden expansion of water contained in the oil droplets during the initial stage of combustion; this increases the contact area of fuel with air and also increases the combustion speed. These facts are likely to contribute to the reduction of thermal NO_x formation. Since water or steam is effective for suppression of soot formation, excess air can be reduced, and the decrease in thermal efficiency is not great. The increase of water concentration in the flue gas is small, so that its influence on metal corrosion can be neglected.

In the fuel emulsion method, usually a slight amount of emulsifying agent is used. Recently, a method that requires no agent has been developed through improvement of the mixer.

The price of a fuel emulsion system is about 50×10^5 to 60×10^5 yen (\$$0.25 \times 10^5$ to \$$0.30 \times 10^5$) for a capacity of 1 kl/hr, and the cost of an emulsifying agent is about 100 yen (\$0.50) per kiloliter.

Since it does not reduce fuel NO_x, this method is useful with low nitrogen oils.

2.5 OTHER METHODS

2.5.1 Change of Fuel

Except for special cases, NO_x concentrations are related to the nitrogen content of the fuel, which decreases in the following order: solid fuels (coal and coke), liquid fuels (petroleum fuel oils), and gaseous fuels (town gas, LNG and LPG).

Emissions from gas burning decrease in the following order: LPG (C_3H_8 and C_4H_{10}), LNG (CH_4), and town gas (synthetic gas with a heating value of about 5,000 kcal/Nm^3).

Hydrodesulfurization of heavy oil, which reduces sulfur content from 2-4 percent to 0.1-0.7 percent, also removes 20-30 percent of nitrogen, which is usually present in a concentration of 0.2-0.3 percent in the oil.

2.5.2 Modification of Firing

It is well-known that tangential firing systems give lower NO_x emissions than front and opposed firing systems, because the flame temperature is lower. This lower temperature is caused by better heat transfer resulting from a larger flame volume.

In small boilers, reversely turned firing is used to reduce NO_x emissions. This type of firing is illustrated in Figure 2-25. NO_x reduction is obtained by recirculation in the flue tube.

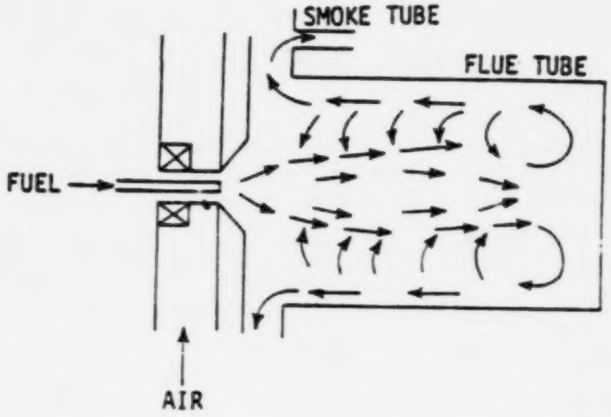

Figure 2-25. Flow pattern in reversely turned firing.

2.5.3 Combination Techniques

Combinations of combustion modification techniques can increase the reduction of NO_x emissions and, therefore, are used widely. However, a combination of techniques based on the same suppression principles, such as the combination of two-stage and off-stoichiometric combustion, is not efficient.

2.6 COMMERCIAL APPLICATION OF COMBUSTION MODIFICATION (CM)[13,14]

2.6.1 Boilers

Table 2-1 shows the total number of boilers in use in 1974 and the total number of boilers using CM techniques in 1977. Most of the boilers with a capacity over 500,000 Nm^3/hr (167 MW equivalent) are utility boilers, while smaller ones are industrial boilers.

TABLE 2-1. TOTAL NUMBER OF BOILERS INSTALLED BY 1974 AND TOTAL NUMBER OF BOILERS WITH COMBUSTION MODIFICATION (CM) IN 1977

Capacity (1,000 Nm^3/hr)	Existing Boilers[a] Total (A)	With CM (B)	B/A (percent)	New Boilers with CM[b]	Total Boilers with CM
Above 500	154	153	99.3	22	175
100-500	331	155	46.8	30	185
40-100	407	72	17.7	9	81
10-40	2,683	41	1.5	24	65
5-10	3,696	18	0.02	11	29
Below 5	72,313				
Total	79,584	439	0.6	96	535

[a] Boilers installed by 1974.

[b] Boilers installed between 1975 and 1977.

The NO_x emission standards were first applied for large stationary sources and have gradually been extended to smaller ones. As a result, the CM application ratio (B/A) is higher with larger boiler capacity.

The number of small boilers using CM may not be very reliable because the research was done mainly for large installations.

NO_x emission levels of boilers before and after the use of CM are given in Table 2-2. The NO_x reduction ratio ranges from 20 to 50 percent with different fuels. New boilers tend to give lower NO_x emissions than do existing boilers, except for boilers using grades A and B oil. The figures for the latter may not be very reliable because of the limited number of boilers investigated.

The types of CM techniques used for boilers are presented in Table 2-3 (low-excess-air combustion is not listed). In general, the low-NO_x burner (LNB), two-stage combustion (TSC) and a combination of two-stage combustion and flue gas recirculation (FGR) are used widely. Over 70 percent of large boilers (over 500,000 Nm^3/hr) use TSC and a combination of TSC and FGR. Many small boilers which have flue gas flow rates under 100,000 Nm^3/hr use low-NO_x burners.

Table 2-4 gives the effects of CM techniques on existing boilers. The combination of two methods (TSC and FGR) and the combination of three methods (LNB, TSC and FGR) give high efficiencies of 42-44 percent. The combination of TSC and FGR is used for a large number of boilers. The reduction ratio with a low-NO_x burner is 27 percent and is equal to that of two-stage combustion. Low-NO_x burners and two-stage combustion are also used widely. Off-stoichiometric combustion (OSC) requires a low investment cost and gives a relatively low NO_x reduction.

Table 2-5 shows typical NO_x levels attainable by CM techniques for large boilers (above 500,000 Nm^3/hr), as indicated by burner and boiler manufacturers. There are a few manufacturers who indicate values 20-30 percent lower than those shown in Table 2-5. Even lower concentrations may be attained for smaller boilers. Comparison of Table 2-5 with Table 2-2 shows that further NO_x abatement may be achieved by CM to a considerable extent for many NO_x sources.

TABLE 2-2. BOILER NO_x EMISSION LEVELS[a] BEFORE AND AFTER COMBUSTION MODIFICATION (CM)

Fuel	Existing Boilers							New Boilers (with CM)		
	Before CM			After CM						
	Max.	Min.	Mean	Max.	Min.	Mean	Reduction Ratio[b]	Max.	Min.	Mean
Coal	800	250	560	650	200	446	20.4	--	--	--
Grade C oil and crude oil	600	100	273	320	80	176	35.5	240	60	162
Grade A and B oils	290	50	134	150	30	77	42.5	150	50	107
Naphtha, kerosene and by-product oil	310	70	233	230	30	117	49.8	110	30	87
Gaseous fuel	250	50	153	170	20	101	34.0	130	30	75

[a] In ppm, corrected to 4 percent O_2 for oil, 5 percent O_2 for gas, and 6 percent for coal.

[b] Reduction ratio = 100 x [(mean before CM-mean after CM)/mean before CM].

TABLE 2-3. NUMBER OF BOILERS WITH COMBUSTION MODIFICATION TECHNIQUES

Capacity (1,000 Nm^3/hr)		LNB[a]	TSC	FGR	OSC	SI	LNB + FGR	TSC + FGR	LNB + TSC + FGR	EF	LNB + TSC	LNB + OSC	Other	Subtotal
Over 500	Existing	4	35	21	0	0	0	73	7	0	4	2	7	153
	New	0	6	0	1	0	0	12	0	0	0	0	3	22
	Subtotal	4(2)[b]	41(23)	21(12)	1(1)	0(0)	0(0)	85(49)	7(4)	0(0)	4(2)	2(1)	10(6)	175(100)
100-500	Existing	38	21	8	12	1	6	15	8	0	25	13	8	155
	New	1	5	2	1	0	0	0	16	0	1	0	4	30
	Subtotal	39(21)	26(14)	10(5)	13(7)	1(1)	6(3)	15(8)	24(13)	0(0)	26(14)	13(7)	12(6)	185(100)
40-100	Existing	33	4	3	13	1	2	2	0	3	3	0	8	72
	New	2	1	1	0	0	1	3	1	0	0	0	0	9
	Subtotal	35(43)	5(6)	4(5)	13(16)	1(1)	3(4)	5(6)	1(1)	3(4)	3(4)	0(0)	8(10)	81(100)
10-40	Existing	11	10	2	1	3	0	2	0	2	2	2	6	41
	New	7	4	5	0	0	0	5	0	0	0	0	3	24
	Subtotal	18(28)	14(22)	7(11)	1(2)	3(5)	0(0)	7(11)	0(0)	2(3)	2(3)	2(3)	9(14)	65(100)
Below 10	Existing	5	0	2	0	1	1	1	0	0	1	0	7	18
	New	9	0	0	0	0	1	0	0	0	1	0	0	11
	Subtotal	14(48)	0(0)	2(7)	0(0)	1(3)	2(7)	1(3)	0(0)	0(0)	2(7)	0(0)	7(24)	29(100)
Total	Existing	91	70	36	26	6	9	93	15	5	35	17	36	439
	New	19	16	8	2	0	2	20	17	0	2	0	10	96
	Subtotal	110(21)	86(16)	44(8)	28(5)	6(1)	11(2)	113(21)	32(6)	5(1)	37(7)	17(3)	46(9)	535(100)

[a] LNB = Low NO_x burner; TSC = Two-stage combustion; FGR = Flue gas recirculation; OSC = Off-stoichiometric combustion; SI = Steam injection; EF = Emulsified fuel.

[b] Figures in parentheses are proportions (percent) in all types.

TABLE 2-4. EFFECTS OF COMBUSTION MODIFICATION TECHNIQUES

Type of CM Technique	Mean Reduction Ratio (percent)	Number of Boilers with CM Techniques
OSC	18	24
LNB	27	80
TSC	27	72
FGR	32	25
LNB + OSC	25	17
LNB + TSC	34	32
TSC + FGR	42	92
LNB + TSC + FGR	44	16
Other	41	31

TABLE 2-5. ATTAINABLE NO_x EMISSION LEVELS (PPM) INDICATED BY BURNER AND BOILER MANUFACTURERS*

Fuel	Existing Boilers	New Boilers
Grades C and B Oil (0.15-0.2 percent N)	130-160	110-120
Gas	100-130	50
Coal	350	300

*Typical values for large boilers, corrected to 4 percent O_2 for oil, 5 percent O_2 for gas, and 6 percent O_2 for coal.

The investment costs for CM techniques are shown in Table 2-6. In general, countermeasures including flue gas recirculation are expensive, while a low NO_x burner and off-stoichiometric combustion are less expensive.

Figure 2-26 illustrates cost performance, that is, the cost of equipment for every percent of reduction ratio, calculated from Tables 2-4 and 2-6. Generally, an expensive countermeasure gives a high NO_x reduction ratio. A low NO_x burner (LNB) is advantageous over two-stage combustion (TSC) because of the lower cost for the same reduction ratio.

2.6.2 Oil Heating Furnaces

Figure 2-27 shows NO_x emission levels of oil heating furnaces using CM. In the same manner as boilers, new furnaces have lower emissions than those of existing ones, and NO_x emissions decrease with low-nitrogen fuels.

CM techniques for oil heating furnaces are shown in Table 2-7. Low-NO_x burners are used widely for both new and existing furnaces regardless of capacity. Fewer CM techniques have been applied to oil heating furnaces than to boilers. The combination of two-stage combustion and flue gas recirculation, used widely for boilers, has not been adopted. The reasons are:

1) The great majority of oil heating furnaces are natural-draft units; therefore, extensive reconstruction is required for the application of the above combination.

2) Low-NO_x burners used in oil heating furnaces combine self-recirculation and two-stage combustion.

TABLE 2-6. INVESTMENT COST FOR COMBUSTION MODIFICATION

Control Technique	Cost (yen/Nm^3/hr)
LNB + TSC + FGR	657 (\$3.29)
LNB + FGR	491 (\$2.46)
TSC + FGR	475 (\$2.38)
LNB + TSC	480 (\$2.40)
TSC	292 (\$1.46)
LNB	129 (\$0.65)*
OSC	26 (\$0.13)
Mean	467 (\$2.34)

*Including change of burner tip.

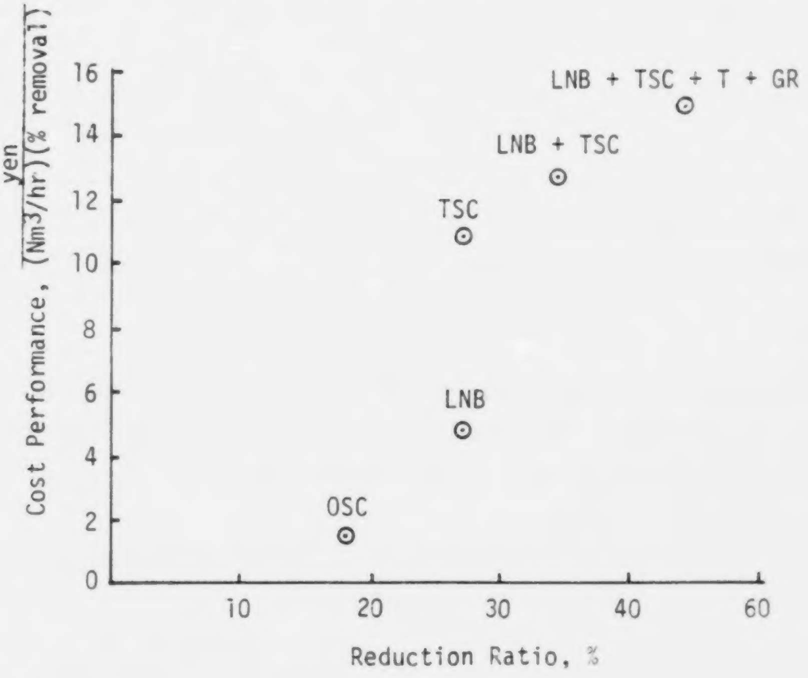

Figure 2-26. Cost performance of NO$_x$ control techniques applied to boilers.

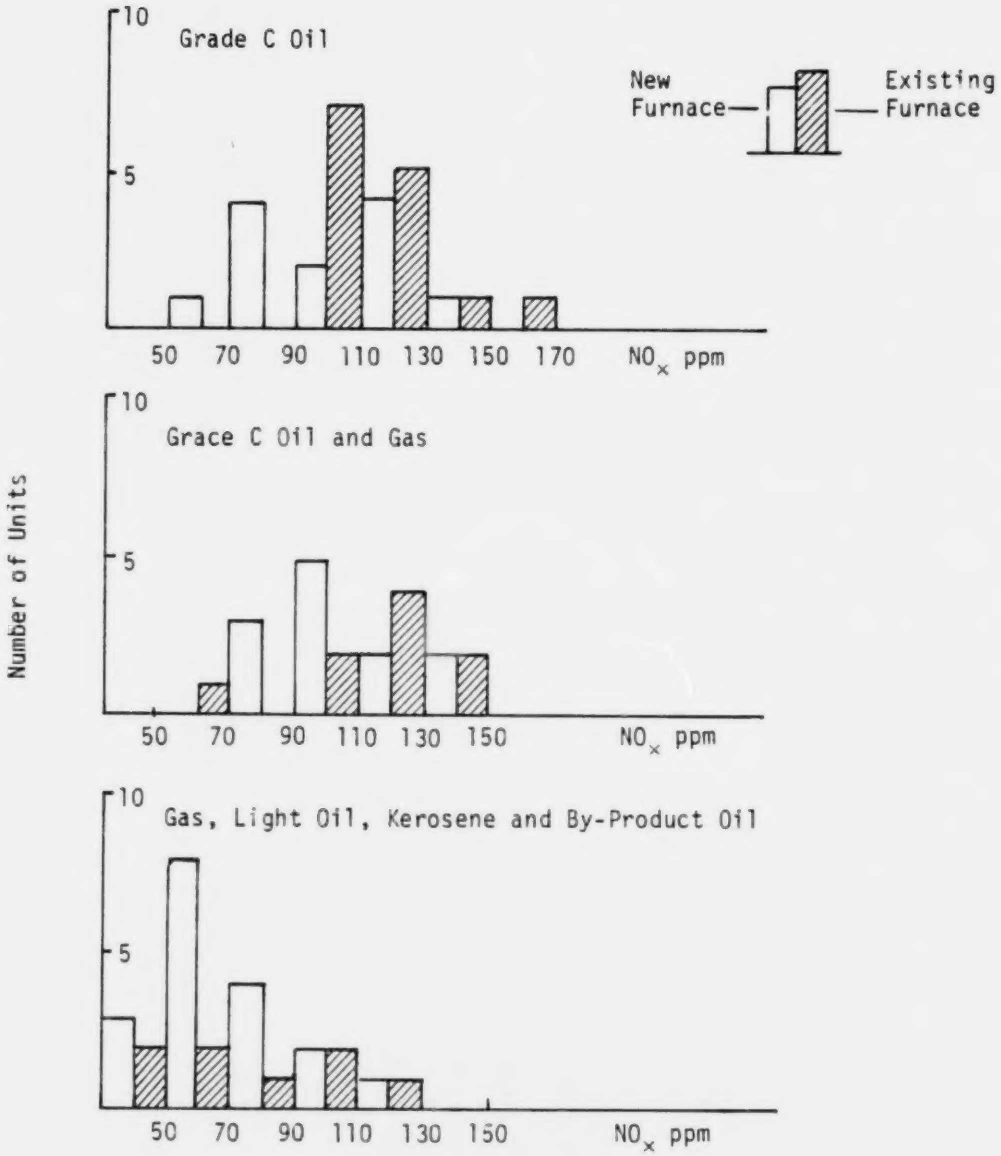

Figure 2-27. NO$_x$ emission levels of oil heating furnaces using CM. (NO$_x$ concentrations are at 11 percent O$_2$)

TABLE 2-7. CM TECHNIQUES USED FOR OIL HEATING FURNACES

Capacity (1,000 Nm^3/hr)		LEA[a]	CF	SI	LNB	FGR	LEA + SI	LEA + LNB	CF + RHL[b]	FGR + RHL	FGR + LNB	LEA + CF + LNB	Subtotal
Above 100	Existing	1	2		2								5
	New				1					1			2
	Subtotal	1(14)	2(29)		3(43)					1(14)			7(100)
40-100	Existing	3	1	2	8	3		1					18
	New		1		11						3	1	15
	Subtotal	3(9)	2(6)		19(58)	3(9)		1(3)			3(9)		33(100)
10-40	Existing	5	3		22		4		1			1	36
	New				17						3		20
	Subtotal	5(9)	3(5)		39(70)		4(7)		1(2)		3(5)	1(2)	56(100)
Below 10	Existing	2		1	5								8
	New				7								7
	Subtotal	2(13)		1(7)	12(80)								15(100)
Total	Existing	11	6	3	37	3	4	1	1			1	67
	New		1		36					1	6		44
	Subtotal	11(10)	7(6)	3(3)	73(66)	3(3)	4(4)	1(1)	1(1)	1(1)	6(5)	1(1)	111(100)

[a] LEA = Low-excess-air combustion; CF = Change of fuel; SI = Steam injection.

[b] RHL = Reduction of heat load.

Table 2-8 shows NO_x levels attainable with the burner for natural draft oil heating furnaces.

TABLE 2-8. NO_x EMISSION LEVELS ATTAINABLE WITH SRG BURNER FOR OIL HEATING FURNACES*

Fuel	NO_x Emission Levels (ppm corrected to 6 percent O_2)
Grade A Oil	70-90
Kerosene	50-60
Gas	50-60

*Heat release rate: 4×10^4 to 8×10^4 kcal/m^3 hr
Furnace temperature: Below 900°C

The investment cost is about an average of 760 yen (\$3.80)/Nm^3/hr for all countermeasures, and about 880 yen (\$4.40)/Nm^3/hr for a low-NO_x burner.

2.6.3 Metal Heating Furnaces

The effects of CM techniques on NO_x reduction with metal heating furnaces using different fuels are presented in Table 2-9. As with boilers and oil heating furnaces, NO_x emission levels are low with metal heating furnaces using low-nitrogen fuels such as naphtha, kerosene and gaseous fuels, while reduction ratios are high.

CM techniques used in metal heating furnaces are shown in Table 2-10. Low-NO_x burners, especially the staged-combustion type, are adopted widely. Steam injection (SI) is used for 10 furnaces with a capacity between 10,000-100,000 Nm^3/hr. This technique is regarded as an emergency measure. In existing small furnaces, emulsified fuels are used because of the ease of adoption.

TABLE 2-9. EFFECTS OF CM TECHNIQUES ON NO_x REDUCTION WITH METAL HEATING FURNACES

Fuel	Before CM (ppm)[1]	After CM (ppm)[1]	Reduction Ratio (percent)
Grade C Oil	228	152	33
Naphtha and Kerosene	171	62	64
Gaseous Fuel[2]	295	87	71
Grade C Oil + Naphtha	138	105	24
Grade C Oil + Gaseous Fuel	200	138	31

[1] Corrected to 11 percent O_2.

[2] Example of high NO_x level before CM.

TABLE 2-10. CM TECHNIQUES USED IN METAL HEATING FURNACES

Capacity 1,000 Nm^3/hr		LNB	TSC	SI	EF*	LNB + TSC	Others	Subtotal
Over 100	Existing	1	0	0	0	0	0	1
	New	0	0	0	0	0	1	1
	Subtotal	1(50)	0(0)	0(0)	0(0)	0(0)	1(50)	2(100)
40-100	Existing	3	0	2	0	0	2	7
	New	0	0	0	0	0	1	1
	Subtotal	3(38)	0(0)	2(25)	0(0)	0(0)	3(38)	8(100)
10-40	Existing	2	0	7	1	2	1	13
	New	1	0	1	0	1	1	4
	Subtotal	3(18)	0(0)	8(47)	1(6)	3(18)	2(12)	17(100)
Under 10	Existing	2	1	0	1	0	1	5
	New	1	0	0	0	0	0	1
	Subtotal	3(50)	1(17)	0(0)	1(17)	0(0)	1(17)	6(100)
Total	Existing	8	1	9	2	2	4	26
	New	2	0	1	0	1	3	7
	Subtotal	10(31)	1(3)	10(31)	2(6)	3(9)	7(20)	33(100)

*EF = emulsified fuel.

The types of applicable CM techniques are limited due to the high flame temperature requirement and the influence of flames on heated materials.

Other techniques, such as low-excess-air combustion, change of fuel, and reduction of heat release rate by furnace reconstruction are also used.

Table 2-11 gives burner manufacturers' test results for metal heating furnaces. Due to the demand by steel makers, the present target of development is about 50 ppm at 11 percent O_2 for low-nitrogen fuels such as grade A heavy oil, kerosene and gaseous fuels. Reduction of burner size is desired to ease the application to existing furnaces.

The investment cost for CM ranges from 20 to 340 yen ($0.10 to $1.70)/$Nm^3$/hr and averages about 210 yen ($1.05)/$Nm^3$/hr. The cost of low-$NO_x$ burners is about 320 yen ($1.60)/$Nm^3$/hr.

TABLE 2-11. BURNER MANUFACTURERS' TEST RESULTS FOR METAL HEATING FURNACES*

Fuel	NO_x Emission Levels (ppm corrected to 11 percent O_2)
Grade C Oil	90
Grade A Oil	50
Gas	50

*Furnace temperature: about 1300°C.

2.7 REFERENCES*

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SECTION 3

GENERAL DESCRIPTION OF SELECTIVE CATALYTIC REDUCTION (SCR)

3.1 INTRODUCTION

3.1.1 Basic Reactions

Ammonia selectively reacts with NO_x in flue gas at elevated temperatures, as shown in equations 3-1 and 3-2. Actually a small amount of oxygen is needed for the reaction as shown in Figure 3-1. Therefore, the reactions are often expressed by equations 3-3 and 3-4. However, the requirement of oxygen might not be stoichiometric and with some SCR catalysts the reactions seem to be better expressed by equations 3-5 and 3-6.

$$4NH_3 + 6NO = 5N_2 + 6H_2O \qquad (3\text{-}1)$$

$$8NH_3 + 6NO_2 = 7N_2 + 12H_2O \qquad (3\text{-}2)$$

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \qquad (3\text{-}3)$$

$$4NH_3 + 2NO_2 + O_2 = 3N_2 + 6H_2O \qquad (3\text{-}4)$$

$$8NH_3 + 10NO + O_2 = 9N_2 + 12H_2O \qquad (3\text{-}5)$$

$$12NH_3 + 8NO_2 + O_2 = 10N_2 + 18H_2O \qquad (3\text{-}6)$$

In addition, the following reactions between ammonia and oxygen can take place at higher temperatures:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \qquad (3\text{-}7)$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O \qquad (3\text{-}8)$$

$$4NH_3 + 4O_2 = 2N_2O + 6H_2O \qquad (3\text{-}9)$$

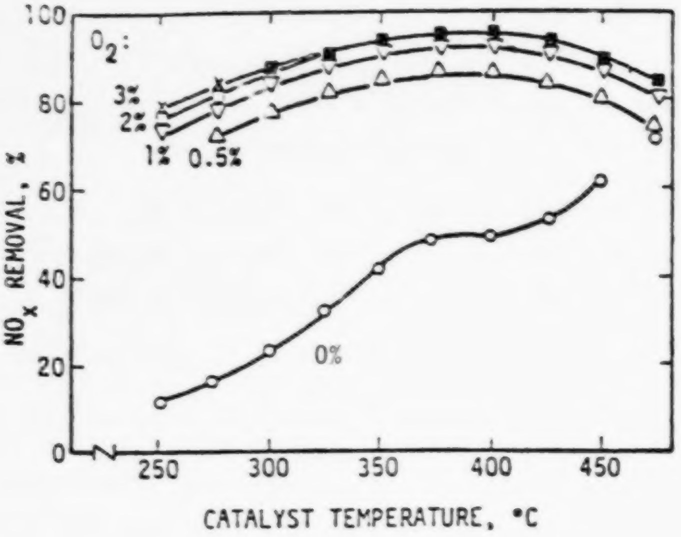

Figure 3-1. Effect of oxygen on NO_x removal (SV, 10,000 hr^{-1}; NO_x, 100 ppm; NH_3/NO_x, 1.0).

Virtually all of the NO_x in combustion gas is present as NO. The optimum temperature for the reaction of NO_x and NH_3 without a catalyst is in a narrow range of 950-1000°C. The reaction rate is low below this temperature, whereas undesirable reactions (equations 3-7, 3-8, 3-9) readily occur at higher temperatures. The use of a catalyst lowers the reaction temperature to 150-450°C and prevents the undesirable reactions. As shown in Figure 3-2, many catalysts have been developed with an optimum reaction temperature of 300-400°C, so that the boiler economizer effluent at 300-400°C can be directly treated.

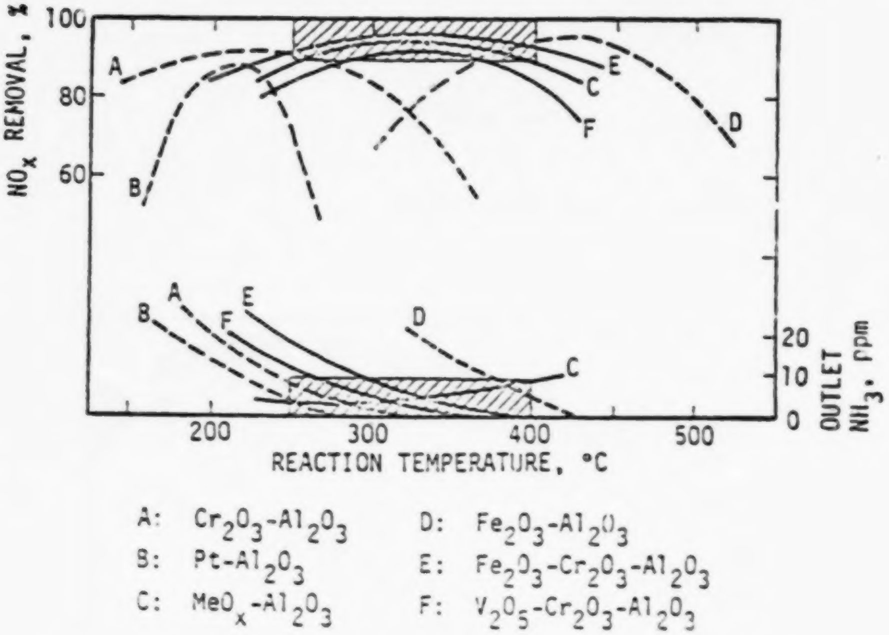

Figure 3-2. Criteria for catalyst for clean gas.[1]

Base metals have been used as the catalyst. Alumina was widely used in the early stage of development as a catalyst carrier, but it is poisoned by SO_x in the gas. Therefore, TiO_2-based, SO_x-resistant catalysts are now used; they will be described in Section 3.2.

Particulate plugging has been the most serious problem for the catalyst, which usually is of granular or pellet type. To cope with this problem, tubular, honeycomb and other specially shaped catalysts and parallel flow type reactors have been developed. These catalysts and reactors will be described in Section 3.3.

3.1.2 Major SCR Plants

SCR has been considered the most useful way to remove NO_x because of its simplicity and its removal efficiency of over 90 percent. Following numerous tests with many pilot plants by many process developers, over 40 commercial SCR units have been constructed. Table 3-1 shows commercial plants and several pilot plants with a capacity of over 10,000 Nm^3/hr (3.3 MW equivalent). Over half the commercial plants use granular catalyst in a fixed bed to treat clean gas from the combustion of LNG, LPG, kerosene, or off gas from the petrochemical industry. The rest of the plants of reactors, to use various types, treat semi-dirty gas from the combustion of low-sulfur oil or dirty gas from the combustion of high-sulfur oil; these plants also include those which treat dirty gas from coke ovens and iron ore sintering machines.

At the early stage of dirty gas treatment, wet-process flue gas desulfurization was applied in advance for gas cleaning (Shindaikyowa P.C. and Kasasaki Steel shown in Table 3-1). The reason for this was that SCR catalysts were apt to be affected by SO_3 and dust in the gas. However, this system is expensive because it requires a large amount of energy to heat the gas cooled by the desulfurization. Since SO_x-resistant catalysts and reactors free from dust plugging were developed later, SCR has been applied in many plants to hot dirty gas without gas cleaning.

3.1.3 Operating Parameters

For 90 percent NO_x removal using granular catalyst, a space velocity (SV)* of 5000-10,000 hr^{-1} and an NH_3/NO_x mole ratio of 0.95-1.2 have been used for dirty gas (see Figure 3-3). For clean gas, however, an SV of 10,000-20,000 hr^{-1} has been applied because a highly reactive catalyst which may be poisoned by SO_x can be used. The SV is usually smaller with parallel flow type reactors which are described in Section 3.3.2.

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*Space velocity equals the ratio of the volume of gas passing through the reactor in an hour at 0°C and atmospheric pressure to the volume of the catalyst bed.

TABLE 3-1. SCR PLANTS (LARGER THAN 10,000 Nm^3/hr)

Process Developer	User	Plant Site	Gas Source	Fuel	Capacity (Nm^3/hr)	Gas Pretreatment	Type of Reactor	Completion
Hitachi, Ltd.	Kawatetsu Chemical	Chiba	Coke Oven	COG, BFG[a]	500,000	ESP[b], H[c]	IMB[d]	Nov 1976
	Chiyoda Kenzai	Kaizuka	Boiler	HO(HS)[e]	15,000	None	IMB	Oct 1977
	Kansai Paint	Amagasaki	Boiler	Kerosene	16,000	H[h]	FB[f]	1977
	Nisshin Steel	Amagasaki	Boiler	HO(LS)[g]	20,000	H	FB	Aug 1977
	Nisshin Steel	Amagasaki	Boiler	HO(LS)	19,000	H	FB	July 1977
	Kansai Electric	Kainan	Boiler	Crude Oil	300,000	None	FB	1977
	Chubu Electric	Chita	Boiler	LNG	2,000,000x2	None	FB	Apr 1978
	Nippon Oils & Fats	Amagasaki	Boiler	HO	20,000	None	IMB	Apr 1978
	Nisshin Steel	Sakai	Boiler	Kerosene	30,000	None	FB	Dec 1978
	Company A	--	Boiler	HO(LS)	490,000	None	FBP[j]	June 1978
	Company B	--	Boiler	HO(LS)	550,000	None	FBP	June 1978
Mitsubishi H.I.	Sumitomo Chemical	Sodegaura	Boiler	HO(LS)	300,000	ESP, HE[i]	IMB	Sept 1976
	Osaka Gas	Takaishi	Boiler	LNG	15,000x2	None	FB	Dec 1976
	Tokyo Electric	Yokosuka	Boiler	HO(LS)	40,000	None	FBP[j]	Mar 1977
	Fuji Oil	Sodegaura	Boiler	HO(LS)	200,000	None	FBH[k]	Jan 1978
	Kyushu Electric	Kokura	Boiler	LNG	1,690,000x2	None	FB	Oct 1978
	Company C	--	Boiler	HO(LS)	1,010,000	None	FBP	Feb 1978
	Company D	--	Boiler	HO(LS)	490,000	None	FBP	July 1978
	Chubu Electric	Chita	Boiler	HO(LS)	1,920,000	None	FBH	Feb 1980
Ishikawajima H.I.	Chubu Electric	Taketoyo	Boiler	Crude Oil	20,000	None	FBH	Apr 1977
	Ajinomoto	Kawasaki	Boiler	HO(LS)	180,000	None	FBH	Jan 1978
	Company E	--	Boiler	HO(LS)	960,000	None	FBH	Apr 1978
	Company F	--	Boiler	HO(LS)	480,000	None	FBH	June 1978
	Chugoku Electric	Kudamatsu	Boiler	Crude Oil	1,000,000	None	FBH	Apr 1979
	Chugoku Electric	Kudamatsu	Boiler	HO(LS)	1,900,000	None	FBH	July 1979
	Tohoku Electric	Niigata	Boiler	HO(LS)	1,660,000	None	FBH	Aug 1981
Hitachi Zosen	Idemitsu Kosan	Chiba	Boiler	CO	350,000	H	FB	Oct 1975
	Shindaikyowa P.C.	Yokkaichi	Boiler	HO(HS)	440,000	ESP, DS[l], HE, H	FB	Nov 1975
	Toshin Steel	[illegible]go	Furnace	Kerosene	71,000	None	FB	May 1976
	Kawasaki Steel	Chiba	SM[m]	Coke, Oil	762,000	DS, ESP, HE, H	FB	Nov 1976
	Nippon Satetsu	Chiba	Furnace	HO	10,000	None	FB	Dec 1976

(Continued)

[a] Coke oven gas, blast furnace gas
[b] Electrostatic precipitator
[c] Heating
[d] Intermittent moving bed
[e] Heavy oil (high sulfur)
[f] Fixed bed
[g] Heavy oil (low sulfur)
[h] Heater
[i] Heat exchanger
[j] Fixed bed parallel plate
[k] Fixed bed honeycomb
[l] Desulfurization
[m] Sintering machine

TABLE 3-1. (Continued)

Process Developer	User	Plant Site	Gas Source	Fuel	Capacity (Nm^3/hr)	Gas Pretreatment	Type of Reactor	Completion
Sumitomo Chemical	Sumitomo Chemical	Sodegaura	Boiler	HO(HS)[a]	30,000	ESP[b]	FB[c]	July 1973
	Higashinihon M.	Sodegaura	Furnace	LPG	200,000	None	FB	May 1974
	Nihon Ammonia	Sodegaura	Furnace	LPG	250,000	None	FB	Jan 1975
	Sumitomo Chemical	Niihama	Furnace	LPG	200,000	None	FB	Apr 1975
	Sumitomo Chemical	Anegasaki	Furnace	LPG	200,000	None	FB	Apr 1975
	Sumitomo Chemical	Anegasaki	Furnace	LPG	100,000	None	FB	
	Maruichi Kokan	Sakai	Furnace	LPG	10,000	None	FB	
	Sumitomo Chemical	Sodegaura	Boiler	HO(MS)[d]	240,000	Wet ESP, HE[f], H[g]	FB	Mar 1976
	Sumitomo Chemical	Sodegaura	Boiler	HO(MS)[d]	300,000	ESP	IMB[i]	Oct 1976
Mitsui Toatsu	Mitsui Toatsu	Takaishi	Furnace	Off Gas	87,000	None	FB	Feb 1976
	Osaka Pet. Chem.	Takaishi	Furnace	Off Gas	91,000	None	FB	Sept 1976
	Mitsui Toatsu	Takaishi	Furnace	Off Gas	170,000	None	FB	Jan 1977
	Nishinihon M.	Takaishi	Furnace	Off Gas	363,000	None	FB	June 1977
	Idemitsu Pet. Chem.	Ichihara	Boiler	Off Gas	300,000	None	FB	Oct 1977
Mitsui Engineering	Mitsui Pet. Chem.	Chiba	Boiler	CO	200,000	ESP	FB	Oct 1975
	Ukishima Pet. Chem.	Chiba	Boiler	HO(LS)[e]	220,000	None	FBT[h]	Apr 1978
Sumitomo Chem. Engineering	Toho Gas	Sorami	Boiler	Naphtha	31,000x2	None	FB	Oct 1977
	Toho Gas	Sorami	Boiler	Naphtha	23,000	None	FB	Dec 1977
	Toho Gas	Sorami	Boiler	Naphtha	23,000	None	FB	June 1978
	Toho Gas	Sorami	Boiler	Naphtha	19,000	None	FB	July 1978
Mitsubishi Kakoki	Nippon Yakin	Kawasaki	Boiler	HO(HS)	14,000	H[g]	FB	July 1978
	Toho Gas	Sorami	Furnace	Naphtha	19,000	None	FB	Oct 1978
	Toho Gas	Kawasaki	Boiler	Kerosene	10,000	None	FB	Nov 1978
	Toho Gas	Chita	Boiler	Kerosene	30,000	None	FB	Oct 1977
	Toho Gas	Chita	Boiler	Kerosene	43,000	None	FB	Oct 1978
J. G. Corp.	Kashima Oil	Kashima	Furnace	HO(MS)	50,000	None	PP[j]	Nov 1975
	Fuji Oil	Chiba	Boiler	CO	70,000	None	PP	July 1976
	Nippon Steel	Kimitsu	Coke Oven	COG	150,000	None	PP	Mar 1977
Asahi Glass	Asahi Glass		Furnace		70,000	None	IMB[i]	
Kobe Steel	Kansai N.K.	Amagasaki	Coke Oven	COG	104,000	None	IMB	Aug 1977
Kurabo	Kurabo	Hirakata	Boiler	HO(HS)	30,000	None	CMB[k]	Aug 1975

[a] Heavy oil (high sulfur)
[b] Electrostatic precipitator
[c] Fixed bed
[d] Heavy oil (medium sulfur)
[e] Heavy oil (low sulfur)
[f] Heat exchanger
[g] Heater
[h] Fixed bed tubular catalyst
[i] Intermittent moving bed
[j] Parallel passage
[k] Continuous moving bed

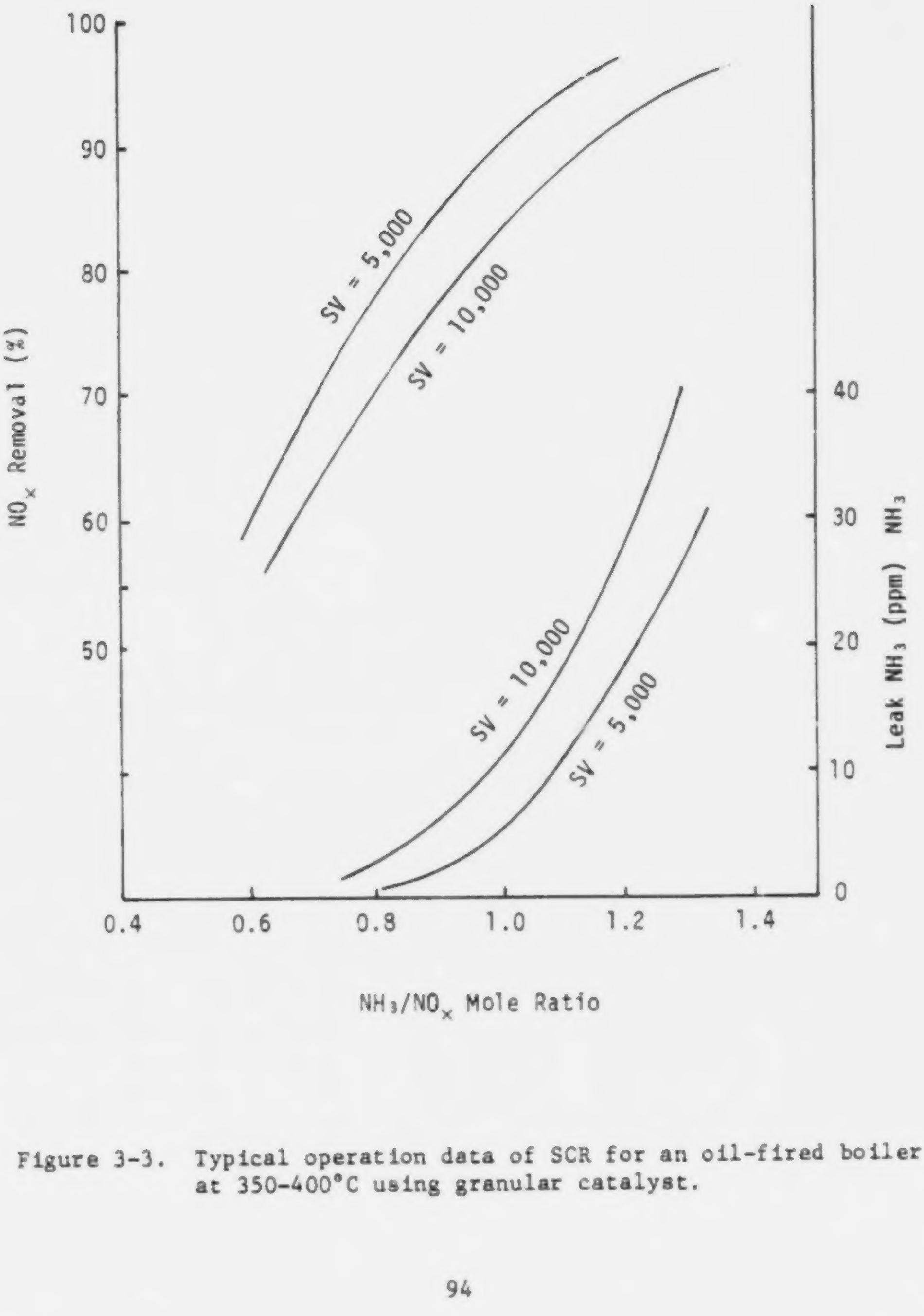


Figure 3-3. Typical operation data of SCR for an oil-fired boiler at 350-400°C using granular catalyst.

The amount of leak ammonia (NH_3 in reactor effluent) is minor when the NH_3/NO_x mole ratio is smaller than 0.8; it is considerable when the ratio is larger than 1.0. The use of a large SV reduces the amount of catalyst, but lowers the NO_x removal efficiency and increases leak ammonia. This is illustrated in Figure 3-3.

The economizer outlet temperature often fluctuates between 270 and 400°C with the boiler load. For clean gas treatment, a drop in the gas temperature does not lower the NO_x removal efficiency when an adequate catalyst is used because the decrease in gas volume can compensate for the lowering of the reaction rate (Figure 3-4). With dirty gas, the situation is similar above about 300°C; below this temperature, however, ammonium bisulfate tends to deposit on the catalyst to lower its activity. For some boilers using sulfur-containing fuel, an auxiliary burner or a bypass system is used to take a portion of the hot gas before it reaches the economizer. In this way the gas temperature is maintained so that no deposit of the bisulfate is formed. The gas heating system is not necessary if the low-temperature period lasts for only several hours, because ammonium bisulfate is removed when the temperature is raised to 350°C.

Low-temperature catalysts reactive at 150-200°C have been developed for gases such as those from iron-ore sintering machines and coke ovens. Also, it is not possible to modify the duct system of some existing boilers to obtain hot gas before the air preheater. Since heating of those gases to above 300°C is costly, requiring a heat exchanger, heater, and much energy, low-temperature catalysts are advantageous. A catalyst developed by Kureha Chemical is reactive at 150°C but is poisoned seriously by SO_x and requires nearly complete desulfurization of the gas in advance. It will be discussed in Section 4.9. A catalyst developed by JGC works at 200°C and is resistant to SO_x. Although ammonium bisulfate deposits on it below 250°C and reduces its activity, occasional heating of the contaminated catalyst to above 350°C removes the bisulfate. This catalyst will be discussed in Section 4.4.

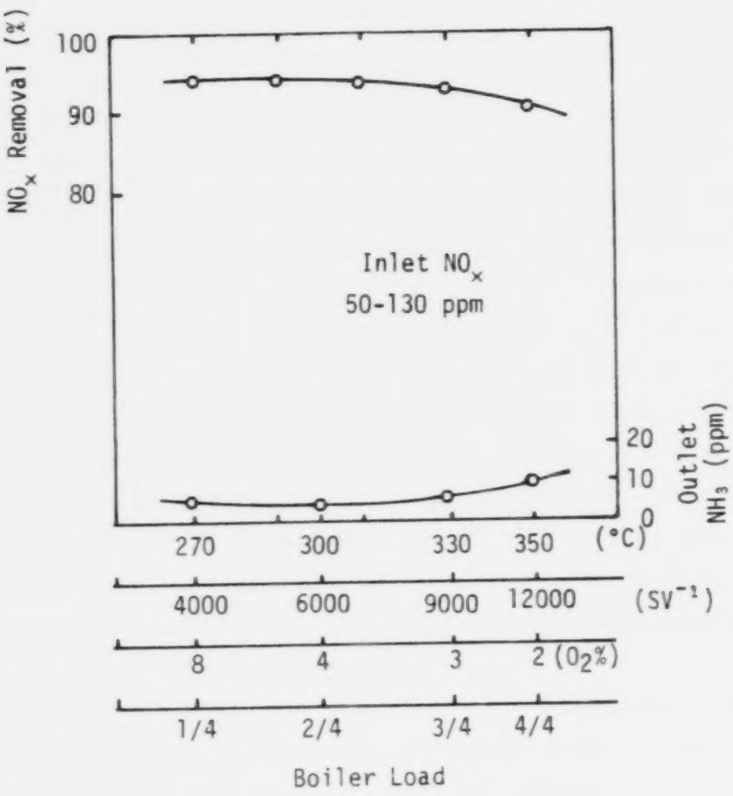


Figure 3-4. Results of clean gas treatment at different boiler loads (NH_3/NO_x = 1.0).[1]

3.2 COMPOSITION AND BEHAVIOR OF CATALYSTS

3.2.1 Introduction

At the early stage of development of SCR, base metal catalysts based on an alumina carrier were used predominantly. As a heat-resistant catalyst carrier, γ-Al_2O_3 has been most popular because of its large surface area and high activity. The surface area of different carriers is generally as shown below:

$$\gamma - Al_2O_3 > TiO_2 > ZrO_2 > MgO > \alpha - Al_2O_3 > SiO_2{}^{3} \qquad (3\text{-}10)$$

A catalyst based on ferric oxide has also been used. However, alumina and ferric oxide have been found to be poisoned by SO_x in flue gas. Pretreatment of flue gas by wet process desulfurization to remove most of SO_x has been carried out in a few commercial plants; this system is very costly, however, because a large quantity of fuel is needed to reheat the gas to a temperature suitable to SCR.

Since a few years ago, titania (TiO_2)-based catalysts have become popular for dirty gas treatment because of titania's resistance to SO_x. The SO_x resistance of the catalyst carrier is shown below:[1]

$$TiO_2 = SiO_2 > \alpha - Al_2O_3 > \eta\text{-}Al_2O_3 > \gamma\text{-}Al_2O_3 \qquad (3\text{-}11)$$

The catalyst metals also tend to react with SO_x, particularly with SO_3. Some of the metals lose activity when reacted with SO_3. Unlike these metals, vanadium compounds are resistant to SO_3. Therefore, many of the SO_x-resistant catalysts are based on TiO_2 and V_2O_5 and are fairly stable against gases containing up to about 2000 ppm of SO_x of which about 100 ppm is present as SO_3. Flue gas from high-sulfur coal contains larger amounts of SO_2 but little SO_3. Currently, catalyst producers guarantee a life of one year for catalysts used to treat such dirty gas.

The SCR reactor effluent contains a small amount of ammonia. In order to reduce the ammonia, ammonia reduction catalyst has been developed by several producers.

3.2.2 Behavior of Al_2O_3 Carrier

Most alumina carriers are in the form of γ-Al_2O_3, which has a large surface area and high activity. The alumina in γ form, however, readily reacts with SO_3 to form $Al_2(SO_4)_3$ to reduce surface area and activity (see Figure 3-5). Even though a gas may contain SO_2 and no SO_3, a portion of SO_2 is oxidized on the catalyst surface to SO_3 and reacts with Al_2O_3. By heating the poisoned carrier to 800°C, $Al_2(SO_4)_3$ is decomposed to regenerate Al_2O_3 and to recover the activity.

$$Al_2O_3 + 3SO_3 = Al_2(SO_4)_3 \tag{3-12}$$

$$Al_2O_3 + 3SO_2 + {}^3\!/_2O_2 = Al_2(SO_4)_3 \tag{3-13}$$

$$Al_2(SO_4)_3 \xrightarrow{800°C} Al_2O_3 + 3SO_2 + {}^3\!/_2O_2 \tag{3-14}$$

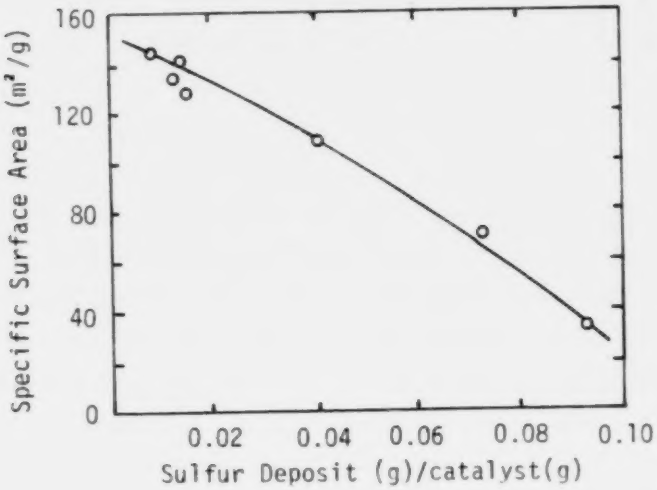


Figure 3-5. Deactivation of catalyst on γ-Al_2O_3 carrier by SO_x.[1]

Since this thermal treatment is costly, however, a more stable form of SO_x-resistant carrier is desired. Calcination of γ-Al_2O_3 at 1100°C produces α-Al_2O_3, which is fairly resistant to SO_x but has a smaller surface area and lower catalyst activity. The change of properties of Al_2O_3 by calcination will be described next.[2]

Three kinds of commercial Al_2O_3 carriers in γ form (two cylindrical and one spherical) were calcined at temperatures between 600 and 1200°C. The changes in physical properties are summarized in Table 3-2. Al_2O_3 was sintered above 750°C resulting in a decrease in pore volume and surface area. The γ type was converted to α type at 1100°C or above. The surface area of the alumina calcined at 1100°C is only one-fifth that calcined at 600°C. Calcination at 1150°C or above further reduced the surface area and catalyst activity remarkably. Figure 3-6 shows the weight increase in Al_2O_3 due to reaction with SO_2; Al_2O_3 calcined at different temperatures was heated at a rate of 2°C/min. in a gas containing either 0.1 percent SO_2 with 5 percent O_2 or 2 percent SO_2 with 10 percent O_2. The weight increase was larger in Al_2O_3 calcined at lower temperatures. The addition of $CuSO_4$ remarkably promoted the increase. It seems that a portion of SO_2 is oxidized to SO_3 on the Al_2O_3 surface and the SO_3 reacts with Al_2O_3 to form $Al_2(SO_4)_3$; $CuSO_4$ promotes this oxidation.

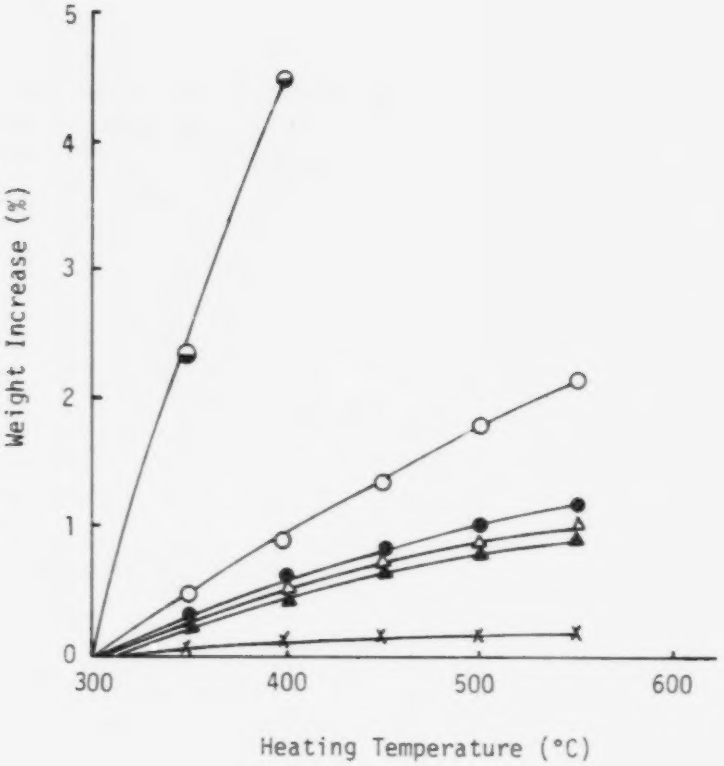
The α type Al_2O_3 prepared by calcination at 1100°C showed only a small weight increase. It may not be feasible, however, to prepare an α type Al_2O_3 carrier of good quality in a large amount, because precise control of the calcination temperature at 1100°C is needed. Below 1100°C the conversion from γ to α is not sufficient and above 1100°C the pore volume and surface area decrease remarkably.

3.2.3 TiO_2-Based Catalysts[2]

TiO_2 is not affected by the SO_x in flue gas. TiO_2, anathase, not only is a good carrier, but also shows catalytic activity by itself. Figure 3-7

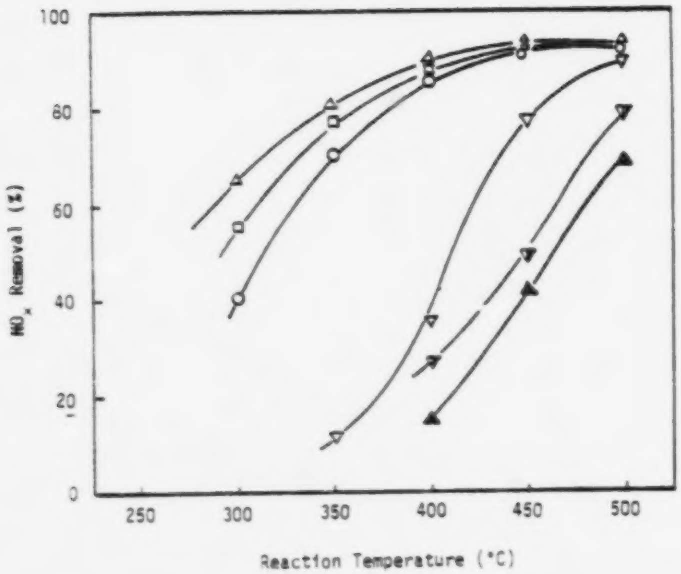
TABLE 3-2. CHANGES IN PHYSICAL PROPERTIES OF Al_2O_3 CARRIERS BY CALCINATION[2]

Sample	Calcination Temp. (°C)	Average Size (mm)		Apparent Density (g/cm^3)	Pore Volume (cm^3/g)	Surface Area (m^2/g)	Average Pore Size (angstroms)
		Diameter	Height				
A (Cylindrical)	600	3.20	3.20	1.30	0.50	150	130
	750					157	
	900	3.18	3.16	1.32	0.49	131	150
	1050	3.00	3.00	1.58	0.37	86	170
	1100	2.85	2.83	1.84	0.32	32	400
	1150	2.78	2.76	1.95	0.26	13	800
	1200	2.69	2.65	2.12	0.21	7	1200
B (Cylindrical)	600	4.83	4.81	1.37	0.46	194	95
	750	4.81	4.82	1.43	0.42	188	90
	900	4.78	4.79	1.43	0.44	123	140
	1100	4.38	4.30	1.79	0.30	29	410
C (Spherical)	600	3.67		1.52	0.38	187	81
	750	3.67		1.45	0.42	183	92
	900	3.60		1.54	0.37	144	100
	1050	3.52		1.65	0.34	92	150
	1100	3.36		1.93	0.25	25	400
	1150	3.19		2.21	0.19	7	1100



Marks	Calcination temp.(°C)	Additive	composition	
			SO_2(%)	O_2(%)
◒	900	$CuSO_4$	2	10
○	900	$CuSO_4$	0.1	5
●	600	None	2	10
△	900	None	2	10
▲	1050	None	2	10
×	1100	None	2	10

Figure 3-6. Weight increase in Al_2O_3 (pre-calcined at 600-1100°C) heated in gas containing SO_2 at rate of 2°C/min.[2]



Mark	Composition (%)			Method of preparation
	Fe_2O_3	TiO_2	Additive	
○	50	50	None	NH_3 was added to $Fe_2(SO_4)_3$-$Ti(SO_4)_2$ soln.
△	40	50	10 MoO_3	NH_3 was added to $Fe_2(SO_4)_3$-$Ti(SO_4)_2$-$(NH_4)_6Mo_7O_{24}$ solution
□	40	50	10 WO_3	NH_3 was added to $Fe_2(SO_4)_3$-$Ti(SO_4)_2$-$(NH_4)_{10}W_{12}O_{41}$ solution
▽	0	100	None	Hydrolysis of $Ti(SO_4)_2$ solution
▼	0	100	None	NH_3 was added to $Ti(SO_4)_2$ solution
▲	0	100	None	Na_2CO_3 was added to $Ti(SO_4)_2$ solution

Figure 3-7. Comparison of NO_x removal from inlet gas* with several TiO_2 based catalysts (calcined at 550°C for 5 hours, 1 mm size).[2]

---

* The gas contained 500 ppm NO, 667 ppm NH_3, 1000 ppm SO_2, and 10 percent O_2; the gas flow was 1000 Ncm^3/hr and the SV, 110,000 hr^{-1}.

shows the results of laboratory tests on TiO_2 and TiO_2-based catalysts in small granules. TiO_2 (anathase) prepared by hydrolysis of $Ti(SO_4)_2$ and calcination at 550°C gave 90 percent NO_x removal at 500°C. Catalyst prepared by sodium carbonate precipitation gave poor results, possibly because of an adverse effect produced by a small amount of sodium contained in the product TiO_2. Catalyst prepared by NH_3 precipitation gave better results than did that from sodium precipitation.

Fe_2O_3-TiO_2 catalyst yielded over 90 percent NO_x removal at 450 and 500°C. Addition of MoO_3 or WO_3 improved the efficiency at lower temperatures. The SV used for the tests is much larger than that used commercially. Use of an SV of about 10,000 with the TiO_2-based catalysts will result in over 90 percent removal above 350°C.

3.2.4 Vanadium Catalysts

Figure 3-8 shows the results of laboratory tests on vanadium catalysts with TiO_2 and Al_2O_3 (γ type). The TiO_2-based catalysts gave a high NO_x removal efficiency between 350 and 400°C and were superior to the Al_2O_3-based catalysts. Catalysts with 10 percent V_2O_5 on a TiO_2 carrier showed the highest efficiency.

Figure 3-9 shows the results of tests to determine catalyst life made by the Government Chemical Research Institute in Tokyo, with V_2O_5 and Fe_2O_3 catalysts on a TiO_2 carrier and flue gas containing 1000 ppm of SO_2. The NO_x removal efficiency, which was nearly 90 percent with both catalysts at the beginning, did not decrease with the V_2O_5 catalyst, but it decreased to about 78 percent with the Fe_2O_3 catalyst in 40 days.

One of the problems with the SCR catalysts is the tendency to oxidize a portion of SO_2 in flue gas to SO_3 which would cause the ammonium bisulfate problem and also might affect the environment. The poisoning of SCR catalysts by SO_2 may also be due to the formation of SO_3 on the catalyst

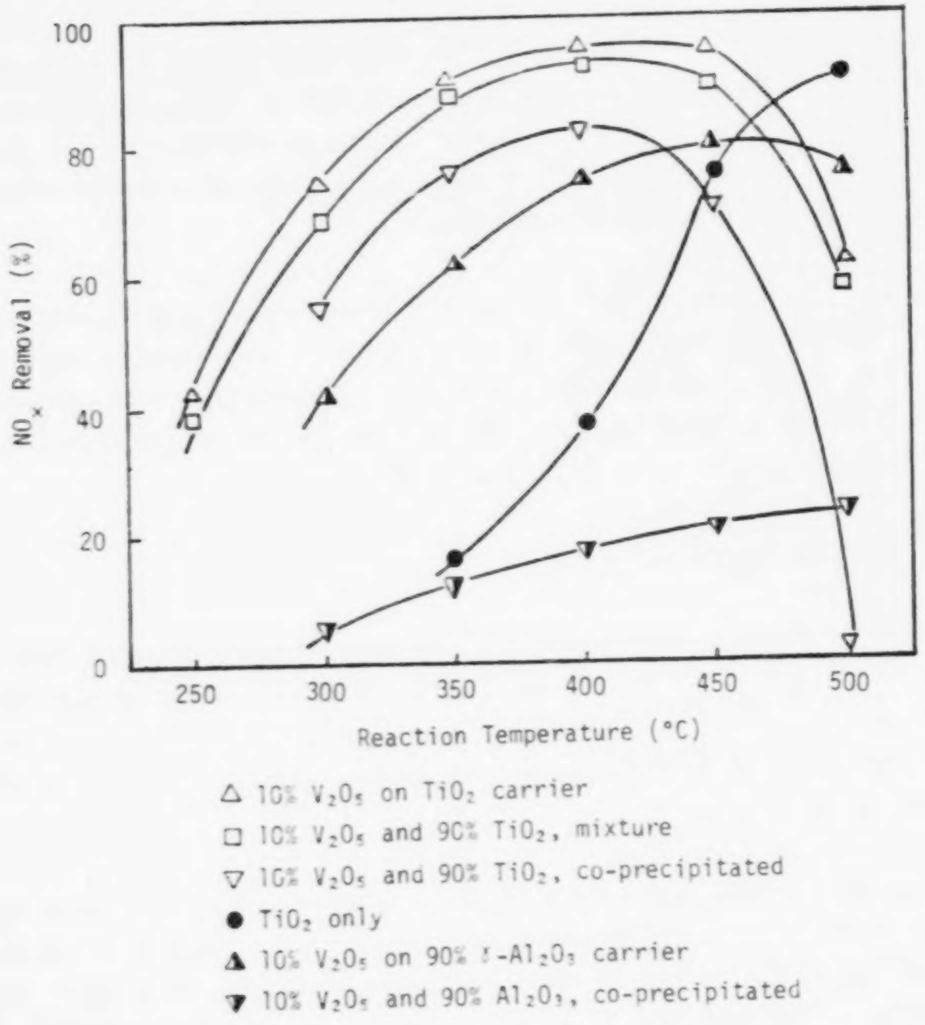
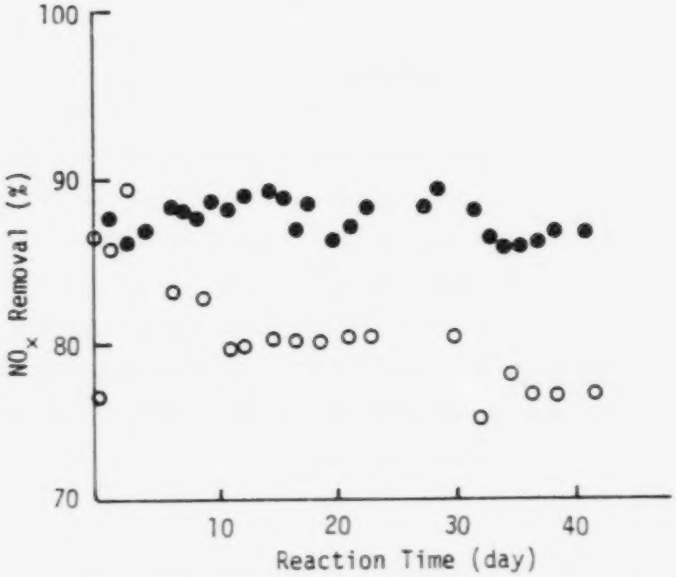


Figure 3-8. Comparison of NO_x removal from inlet gas* with several catalysts (calcined at 550°C for 5 hours, 1 mm size).[2]

---

* The gas contained 500 ppm NO, 667 ppm NH_3, 1000 ppm SO_2, 5 percent O_2 and 10 percent H_2O, N_2 balance; the gas flow was 100 Ncm^3/min and the SV 110,000 hr^{-1}.



SV: 10000 hr^{-1}
NO: 200 ppm
NH$_3$: 200 ppm
SO$_2$: 1000 ppm

O$_2$: 15%
H$_2$O: 10%
Temp: 350°C

○ Fe$_2$O$_3$ - TiO$_2$
● V$_2$O$_5$ - TiO$_2$

Figure 3-9. Results of life tests with TiO$_2$-based catalysts.[3]

It is possible that the vanadium catalyst has a relatively large capability for oxidation; vanadium has been used as oxidation catalyst to convert SO_2 to SO_3 in sulfuric acid plants. The presence of ammonia, a reducing agent, may depress the oxidation considerably. Further studies are needed on this oxidation and its prevention.

3.2.5 Ammonia Decomposition Catalysts

Ammonia decomposition catalysts have been produced by several companies. Results of tests on the catalysts with clean gas are shown in Figure 3-10. The SCR reactor had an NO_x removal efficiency of about 90 percent and the reactor effluent contained about 10 ppm of NH_3. By adding an ammonia converter, the NH_3 concentration was reduced to below 3 ppm and the NO_x removal efficiency increased to over 97 percent; the decomposition catalyst not only decomposes ammonia, but also promotes the reaction of NO_x and NH_3 in the gas.

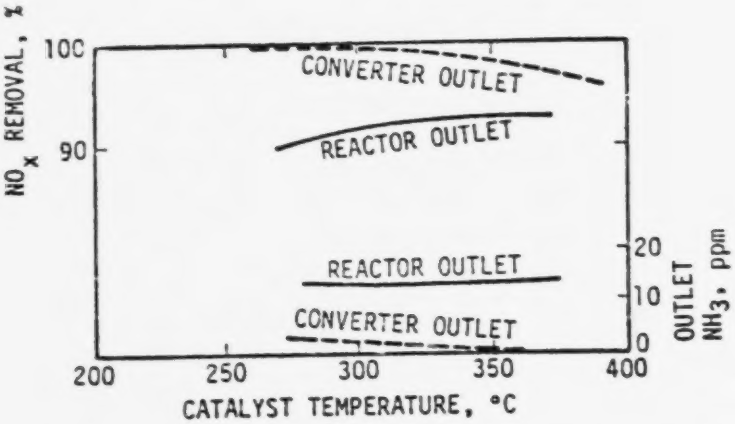


Figure 3-10. Effects of an ammonia converter on NO_x removal from inlet gas* with ammonia decomposition catalysts.[1]

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* The gas contained 150 ppm NO_x, the NH_3/NO_x mole ratio was 1.0, and the gas flow was 12,000 Nm^3/hr.

On the other hand, the decomposition catalyst and the converter have the following disadvantages: 1) Not only the investment cost, but also the pressure drop of the gas (and consequently the power requirement) is increased. 2) Most of the ammonia decomposition catalysts are subject to poisoning by SO_x. 3) The catalysts tend to convert a portion of SO_2 to SO_3. Most of them are oxidizing catalysts and the absence of ammonia is favorable to the oxidation.

The amount of ammonia decomposition catalyst is about a half that of the SCR catalyst. Therefore, the use of the decomposition catalyst is not popular. Process users prefer to reduce leak NH_3 to below about 5 ppm by reducing the NH_3/NO_x mole ratio to 0.9 to obtain an NO_x removal efficiency of 80-85 percent. When a higher NO_x removal efficiency is needed, a larger amount of SCR catalyst and a mole ratio of about 0.95 may be used.

3.2.6 Problems and Further Studies Required

SCR catalysts have been considerably improved. Currently most catalysts have a life of over 2 years when used on clean gas, 1-2 years on semi-dirty gas, and 1 year on dirty gas. The catalysts, however, still present the following problems which remain to be studied and solved.

1) Many dirty gases at a high temperature contain appreciable amounts of compounds in the vapor phase, such as vanadium in oil-fired boiler flue gas and alkaline compounds in the gases from a glass melting furnace, cement kiln, and iron-ore sintering machine. In the liquid or solid phase, those compounds tend to deposit even on catalysts of the parallel flow type, on which solid particles in the gas do not deposit. (This will be discussed further in Section 3.3.) The deposits affect the catalysts in various ways. Vanadium rarely lowers the catalyst activity, but can change the optimum reaction

temperature. Alkaline compounds lower the activity remarkably. Although most of the alkaline compounds can be removed by water-wash, the catalyst is usually degraded to some extent.

2) Fine particulates smaller than about 1 micron tend to enter the small pores of the catalyst carrier, reducing the activity slowly. This "blinding" can not be avoided even in the parallel flow type reactors.

3) Most of the SCR catalysts oxidize below about 2 percent of SO_2 to SO_3. The oxidation ratio may be higher when the gas contains little ammonia.

4) The ammonia decomposition catalyst tends to be poisoned by SO_x. Moreover, it might convert SO_2 to SO_3 to a considerable degree.

5) Most of the catalysts use heavy metals. Caution is needed in disposing of the spent catalyst.

3.3 CATALYST SHAPE AND REACTOR

3.3.1 Introduction

Particulate plugging has been the largest problem for catalysts. For clean gas containing less than about 30 mg/Nm^3 of particulates, a simple type of reactor, with granular or ring tube catalyst in a fixed bed, can be used without appreciable problems. Particulate-rich gases may be treated by an electrostatic precipitator (ESP) to reduce the particulate content to 30 mg/Nm^3. However, since about 400°C is suitable for SCR, a hot ESP is needed which is considerably more expensive than a cold ESP. The hot ESP is useful for low-sulfur coal whose fly ash is not efficiently caught by a cold ESP. A hot ESP, however, is not always highly efficient for particulates from high-sulfur fuels. Therefore, it is sometimes desirable to apply SCR to a praticulate-rich gas.

For this purpose, moving bed and parallel flow type reactors have been developed. (See Figure 3-11 and Table 3-3.) The moving bed reactor uses a granular catalyst, which is charged from the top of the reactor and is moved down intermittently or continuously while the gas is passed through the catalyst layer in a cross flow; this is shown in Figure 3-12. The granular catalyst discharged from the bottom of the reactor is screened to remove particulates and is returned to the reactor. If needed, the catalyst is heated to 700-800°C to eliminate sulfur compounds and carbon before it is returned to the reactor.

The moving bed can treat gases containing less than about 300 mg/Nm^3 of particulates, such as flue gas from an oil-fired boiler. For gases containing 30-100 mg/Nm^3 of particulates, an intermittent moving bed may be suitable to control pressure drop (Figure 3-13), while a continuous moving bed may be preferable for gases with 100-300 mg/Nm^3 of particulates. Flue gas from a coal-fired boiler containing about 20 g/Nm^3 of particulates must first be treated with an electrostatic precipitator or other means to reduce the particulate content to below 300 mg/Nm^3.

On the other hand, the parallel flow type reactor uses a fixed bed of different types of catalyst (honeycomb, plate, and tube) or a parallel passage device (Figure 3-14). The gas passes through a clearance between the parallel layers of the catalyst, and the reactor is expected to be able to handle gas from a coal-fired boiler even without previous dust removal.

In Japan, several intermittent moving bed reactors have been in commercial use for flue gas from oil-fired boilers and coke ovens. Two relatively small commercial plants (17-23 MW equivalent) with parallel passage reactors for oil-fired industrial boilers and two medium-size

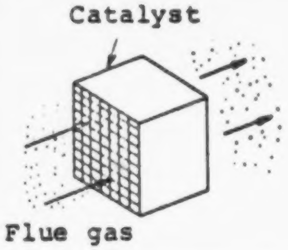
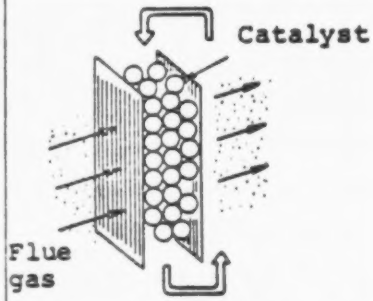
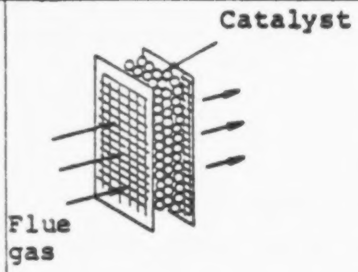
Sort of flue gas	Reactor type	Catalyst shape	Principal structure
Dirty gas	(A) Fixed bed type (Parallel) Flow	Honeycomb-type catalyst	 Catalyst Flue gas
	(B) moving bed type	Pellet type catalyst	 Catalyst Flue gas
Clean gas (LNG, LPG, and naphtha firing)	(C) Fixed bed type	Pellet type catalyst	 Catalyst Flue gas

Figure 3-11. Types of reactors.

TABLE 3-3. REACTORS FOR DUSTY GAS TREATMENT

Type	Process Developer	User	Plant Site	Gas Source	Fuel	Capacity (Nm³/hr)	Completion
Moving Bed	Hitachi Ltd.	Kawatetsu Chemical	Chiba	Coke Oven	COG/RFC[a]	500,000	Nov 1976
	Hitachi Ltd.	Chiyoda Kenzai	Kaizuka	Boiler	HO(HS)[b]	15,000	Oct 1977
	Hitachi Ltd.	Nippon Oils & Fats	Amagasaki	Boiler	HO	20,000	Apr 1978
	Mitsubishi H.I.	Sumitomo Chemical	Sodegaura	Boiler	HO(LS)[c]	382,000	Sept 1976
	Kobe Steel	Kansai H.K.	Amagasaki	Coke Oven	COG	104,000	Aug 1977
	Kurabo	Kurabo	Hirakata	Boiler	HO(HS)	30,000	Aug 1975
	Asahi Glass	Asahi Glass		Furnace		70,000	
Honeycomb	Mitsubishi H.I.	Fuji Oil	Sodegaura	Boiler	HO(LS)	200,000	Jan 1978
	Mitsubishi H.I.	Chubu Electric	Chita	Boiler	HO(LS)	1,920,000	Feb 1980
	Ishikawajima H.I.	Chubu Electric	Taketoyo	Boiler	Crude Oil	20,000	Apr 1977
	Ishikawajima H.I.	Ajinomoto	Kawasaki	Boiler	HO(LS)	180,000	Jan 1978
	Ishikawajima H.I.	Company E	--	Boiler	HO(LS)	960,000[d]	Apr 1978
	Ishikawajima H.I.	Company F	--	Boiler	HO(LS)	480,000[d]	June 1978
	Ishikawajima H.I.	Chugoku Electric	Kudamatsu	Boiler	Crude Oil	1,000,000	Apr 1979
	Ishikawajima H.I.	Chugoku Electric	Kudamatsu	Boiler	HO(LS)	1,900,000	July 1979
	Ishikawajima H.I.	Tohoku Electric	Niigata	Boiler	HO(LS)	1,660,000	Aug 1981
Parallel Passage	JGC	Kashima Oil	Kashima	Furnace		50,000	Nov 1975
	JGC	Fuji Oil	Chiba	Boiler	CO	70,000	July 1976
	JGC	Nippon Steel	Kimitsu	Coke Oven	COG	150,000	Mar 1977
Parallel Plate	Mitsubishi H.I.	Tokyo Electric	Yokosuka	Boiler	HO(LS)	40,000	Mar 1977
	Mitsubishi H.I.	Company C	--	Boiler	HO(LS)	1,010,000	Feb 1978
	Mitsubishi H.I.	Company D	--	Boiler	HO(LS)	490,000	July 1978
	Hitachi, Ltd.	Company A	--	Boiler	HO(LS)	490,000	June 1978
	Hitachi, Ltd.	Company B	--	Boiler	HO(LS)	550,000[d]	June 1978
Tube	Mitsui Engineering	Ukishima Pet. Chem.	Chiba	Boiler	HO(LS)	220,000	Apr 1978

[a] Coke oven gas/refinery off gas.
[b] Heavy oil (high sulfur).
[c] Heavy oil (low sulfur).
[d] Combination with selective noncatalytic reduction.

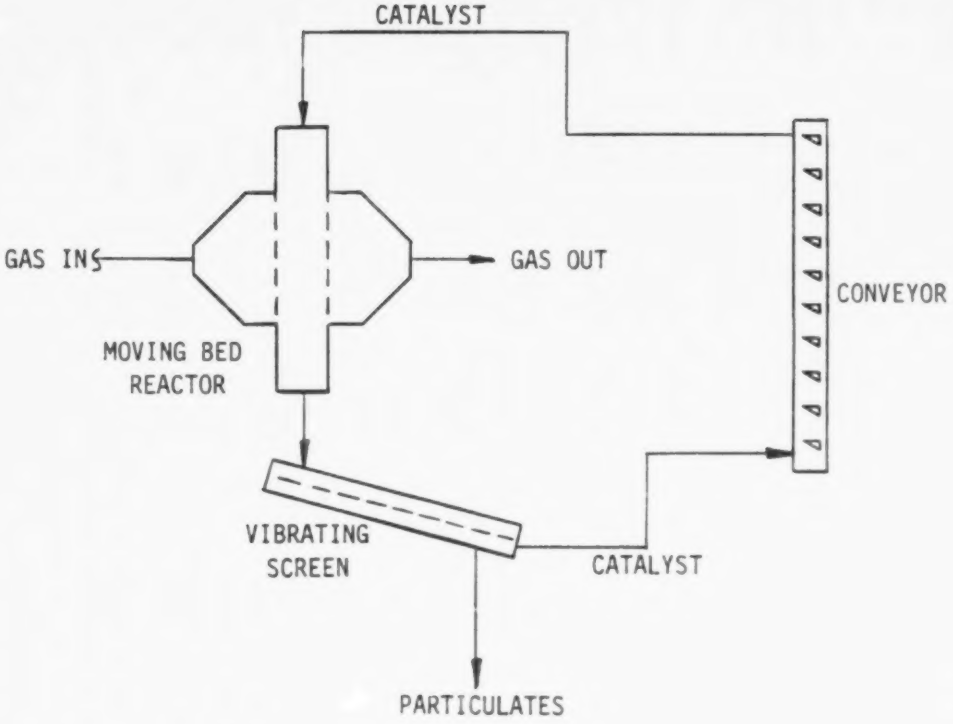

CATALYST
GAS IN
GAS OUT
CONVEYOR
MOVING BED
REACTOR
VIBRATING
SCREEN
CATALYST
PARTICULATES

Figure 3-12. Moving bed reactor.

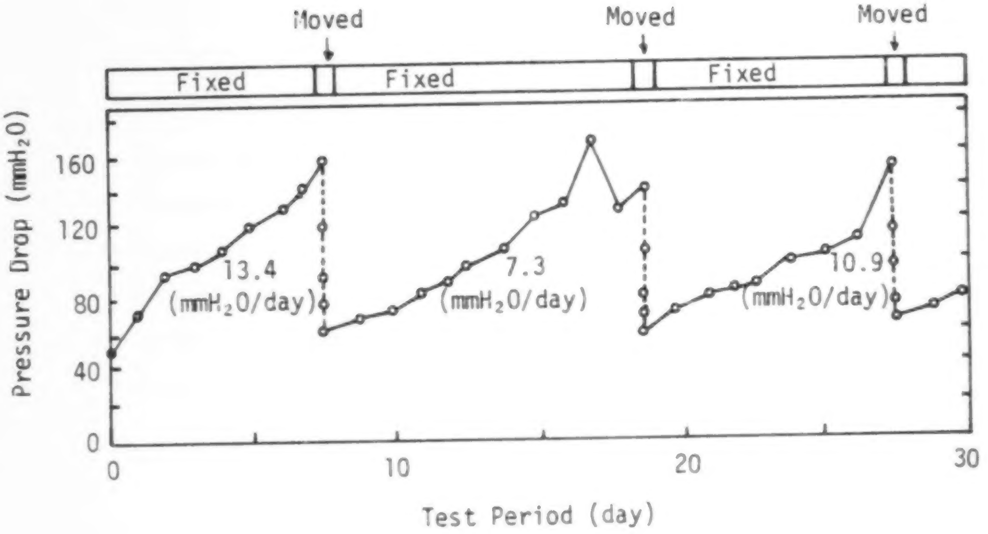
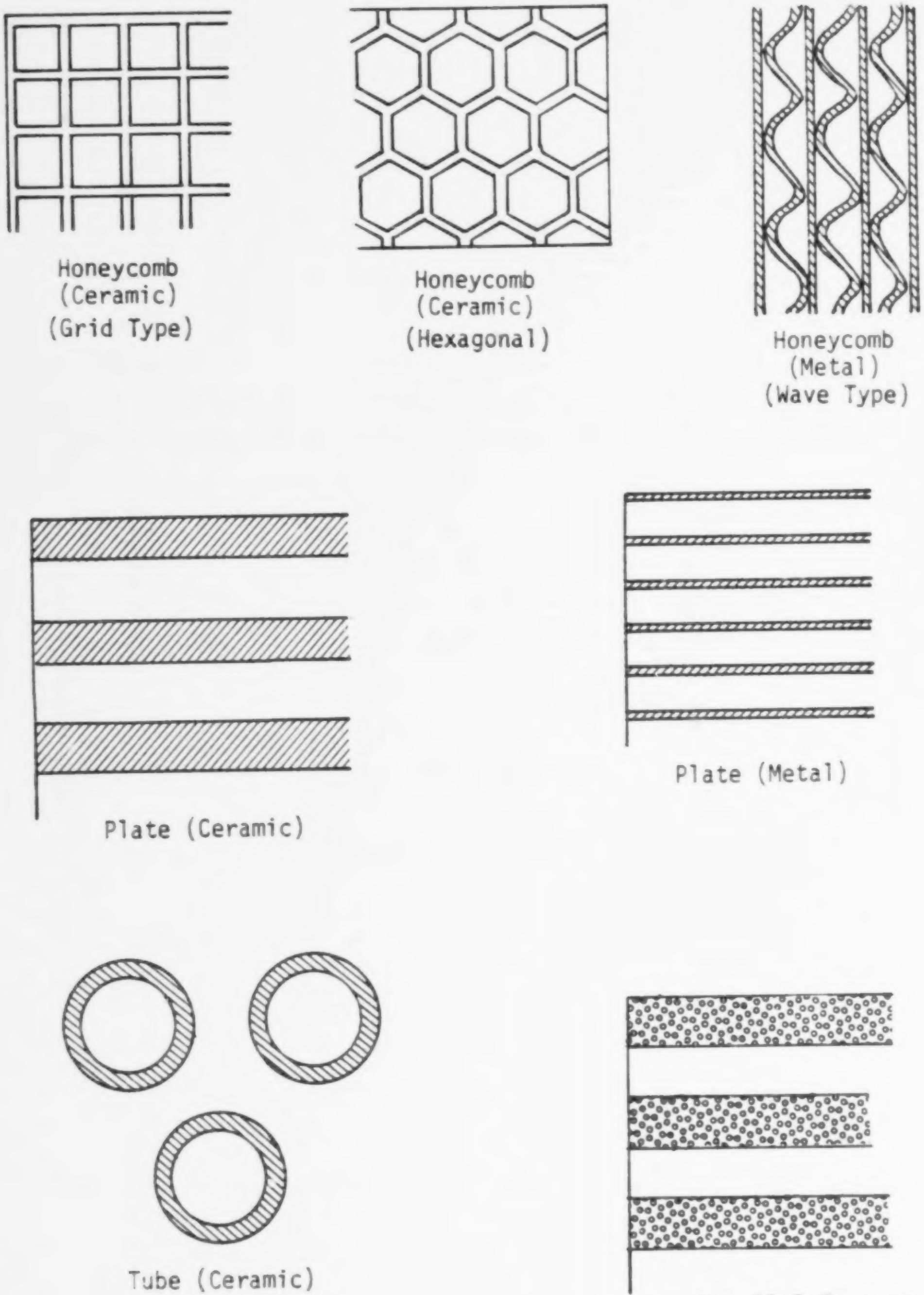


Figure 3-13. Change of pressure drop with an intermittent moving bed.[1]



Honeycomb (Ceramic) (Grid Type)

Honeycomb (Ceramic) (Hexagonal)

Honeycomb (Metal) (Wave Type)

Plate (Ceramic)

Plate (Metal)

Tube (Ceramic)

Parallel Passage

Figure 3-14. Cross sections of parallel flow catalysts (actual sizes).

commercial plants (a 63 MW one using a tubular catalyst and a 73 MW one with a honeycomb catalyst) were put into operation. Many larger plants with honeycomb and plate catalysts started operation recently. (See Table 3-3.)

3.3.2 Moving Bed and Parallel Flow Reactors

Moving bed reactors have the following characteristics, advantages and disadvantages as compared with parallel flow type reactors:

1) Catalysts can easily be replaced during the operation of the denitrification plant.

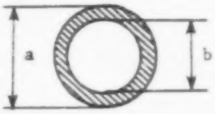
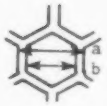
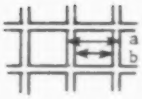
2) A considerable portion of particulates in the gas is removed by the moving bed. For example, 100 mg/Nm^3 at the inlet can be reduced to 30 mg/Nm^3. Most of the collected particulate is separated from the catalyst by screening.

3) The moving bed catalyst is granular and is considerably cheaper than that for most of the parallel flow type reactors. The catalyst can be packed easily in the reactor.

4) The moving bed catalyst is packed fairly densely and has a large surface area per packed volume (Table 3-4).

5) A small gas velocity (0.5-1.5 m/sec) is used to maintain a small pressure drop (Table 3-5). Therefore, for treating a large amount of gas, a special reactor design is needed to obtain a large gas flow area and to keep a uniform gas flow (Figure 3-15).

TABLE 3-4. SPECIFIC SURFACE AREA OF CATALYSTS

	Dimension (mm)		Specific Surface Area (m^2/m^3)	
			Surface Area / Catalyst Volume	Surface Area / Packed Volume
Granule (Sphere)	Diameter			
	4		1500	1100
	6		1000	740
	8		750	555
	10		600	444
Tube*	a	b		
	10	7	1350	405
	15	10.5	900	270
	20	14	677	203
	25	17.5	543	163
	33	23.1	410	124
Honeycomb	a	b		
	9	7	1866	437
	10	7	1204	387
	14	10	908	278
	20	14	602	193
	a	b		
	7	5	1819	556
	10	7	1204	388
	14	10	909	277
	20	14	601	194
Parallel Plate	Thickness	Clearance		
	1	5	2000	320
	1	8	2000	220
	8	8	250	125
	10	12	200	91

* Optimum separate packing (Section 4.5).

TABLE 3-5. COMPARISON OF CATALYSTS AND REACTORS[a]

	Moving Bed	Honeycomb (Metallic)	Honeycomb, Tube (Ceramic)	Parallel Passage	Parallel Plate (Ceramic)	Parallel Plate (Metallic)
Catalyst Size (mm)						
Diameter	4-8[b]					
Thickness		0.5-1	1.5-3	7-10[e]	8-10	1
Opening		4-8	6-20	7-10	8-14	5-10
Gas Velocity (m/sec)[c]	0.5-1.5	2-6	5-10	5-10	5-10	4-8
Bed Depth (m)	0.2-0.6	1-2	1.5-5	3-5	4-6	2-5
SV (1000 hr^{-1})[d]	5-10	5-8	4-8	3-5	1.5-3	2-5
Pressure Drop (mmH_2O)[f]	40-80	30-80	40-140	80-140	80-160	60-120

[a] 90% NO_x removal at an NH_3/NO_x ratio of 1.1 and a temperature of 350-400°C for dirty gas.

[b] Ring type catalysts with larger diameters are also used.

[c] Velocity at 350-400°C in open column (superficial velocity).

[d] Gas volume (Nm^3/hr)/catalyst bed volume (m^3).

[e] Thickness of envelope.

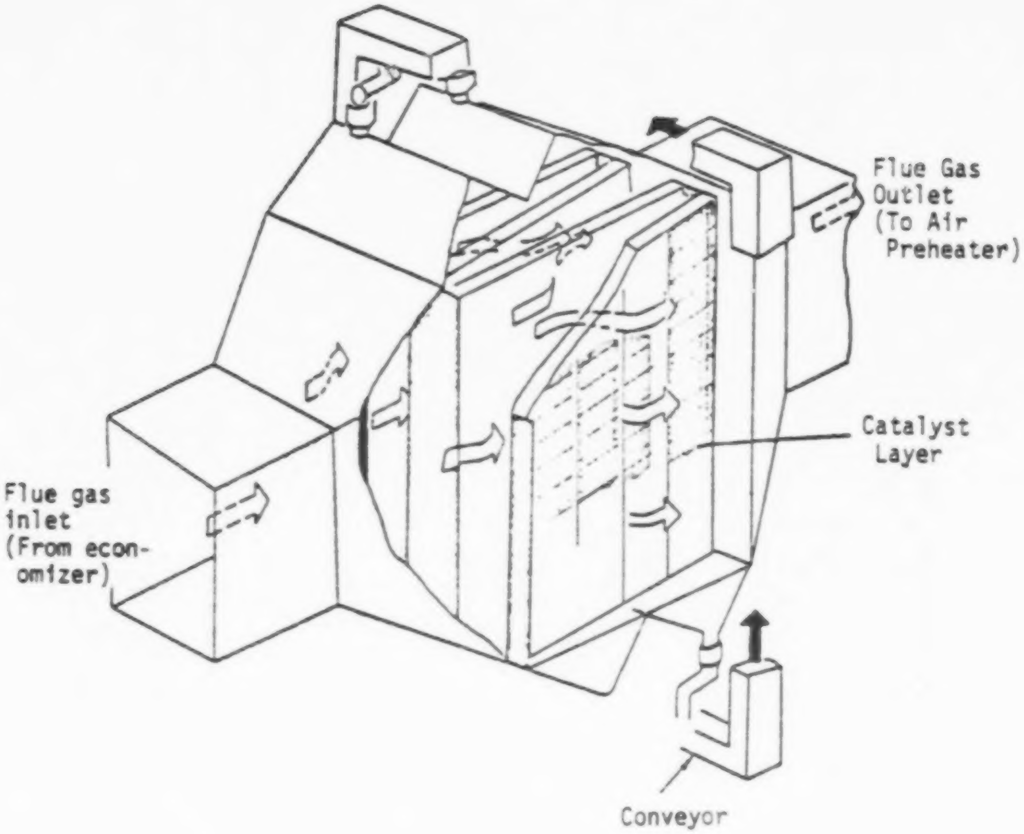

Flue Gas Outlet (To Air Preheater)
Catalyst Layer
Flue gas inlet (From economizer)
Conveyor

Figure 3-15. Moving bed type reactor for a large amount of gas.

6) It is not easy to treat gases containing more than 200 mg/Nm^3 of particulates. Particulate removal is needed in advance for dusty gas.

7) Attrition of catalyst and mechanical trouble with the catalyst transportation system can occur. Attrition is minimized by the use of a hard spherical catalyst.

8) Very fine particulates may enter the small pores of the catalyst and gradually reduce its activity. Although the pore blinding would occur also in the parallel flow type catalysts, the problem might be more serious with the moving bed.

On the other hand, the parallel flow type reactor has the following common characteristics, advantages, and disadvantages:

1) Gases with a large amount of particulate, such as coal-fired boiler flue gas containing 20 g/Nm^3 of fly ash, can be treated, using parallel flow.

2) A catalyst with large openings (gas passing channels over about 7 mm) is safe for dust plugging. With such catalyst, a large gas velocity, normally 5-10 m/sec, is used in order to give a slight plug flow and to raise the NO_x removal efficiency (Table 3-5).

3) A large gas passing area (necessary for the moving bed) is not required, while the depth of the bed is much deeper.

4) The large gas velocity and the deep bed tend to give a large gas pressure drop (80-140 mmH_2O) for some parallel flow reactors in order to attain a high NO_x removal. By using a honeycomb with thin walls and small openings (4-5 mm) and a moderate gas velocity

(2-3 m/sec), a high NO_x removal efficiency is obtained with a small pressure drop (30-50 mmH_2O) but the possibility of dust plugging is greater than with a honeycomb with larger openings.

5) It is difficult to replace the catalyst without stopping plant operation.

6) It is necessary to provide regular spacing of the catalyst during replacement. Usually, tube, plate or honeycomb catalyst is regularly spaced in containers about 1 m x 1 m x 1 m in size, and the containers are placed regularly in the reactor (Figure 3-16). Packing of the catalyst and setting of the containers requires considerable time and labor.

7) Catalyst erosion by particulates can occur at a large gas velocity, particularly when good, regular packing is not achieved.

8) In a large reactor it is not very easy to distribute gas uniformly to each catalyst container; this differs from granular catalyst in a moving and fixed bed, where the bed itself helps to distribute gas uniformly.

9) The parallel flow type catalyst may be placed in a duct between the boiler economizer and air preheater without installing a separate reactor.

3.3.3 Comparison of Parallel Flow Type Catalysts and Reactors

Parallel flow type catalysts and reactors with different characteristics have been developed (Tables 3-4 and 3-5). For commercial use, the most suitable one should be selected on the basis of such characteristics as removal efficiency required, composition of the gas, properties and amount of particulates.

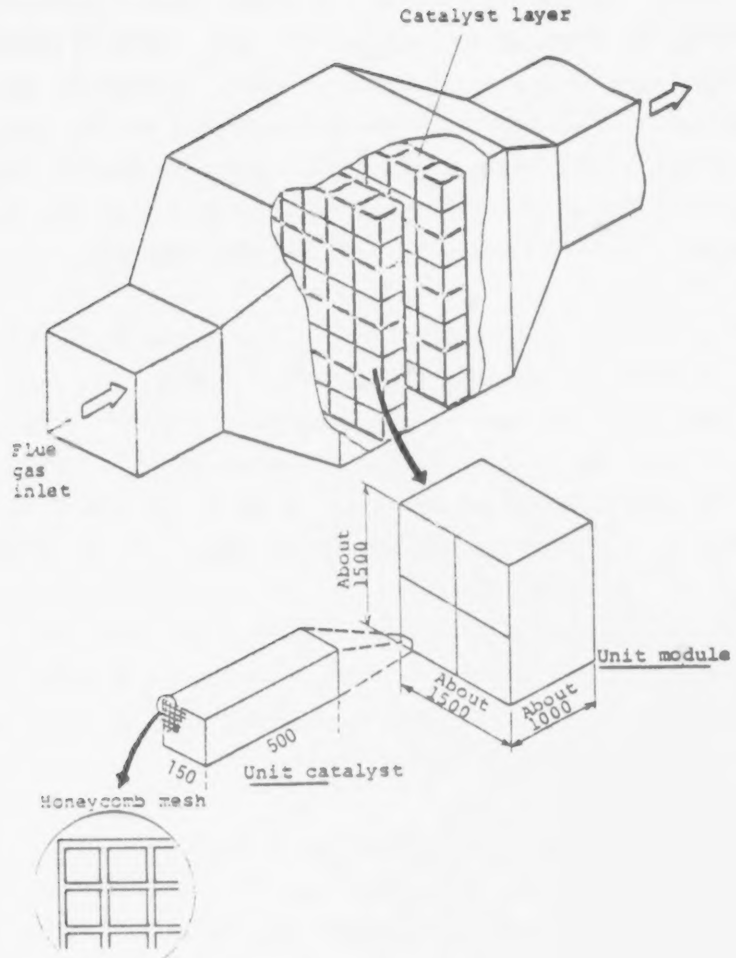

Catalyst layer
Flue gas inlet
About 1500
Unit module
About 1500
About 1000
500
150
Unit catalyst
Honeycomb mesh

Figure 3-16. Example of a fixed bed reactor with honeycomb type catalyst (Ishikawajima-Marima Heavy Industries; sizes are in mm).

Of the parallel flow type catalysts and reactors, the parallel plate may be the simplest and the least vulnerable to dust plugging. The plates are made of either ceramic or metallic material; they are 50-100 cm square with thicknesses of about 10 mm with ceramic and 1 mm with metallic material. The plates are positioned in a basket in parallel with 5-10 mm clearance (Figure 3-14), and the baskets are placed in the reactor. The ceramic plate may not be highly efficient because it must be made fairly thick to maintain enough strength; generally only a thin surface of the catalyst (about 0.5 mm) is actually used for the reaction.

The metallic plate with about 1 mm thickness may be fairly efficient when used with a small clearance (see Tables 3-4 and 3-5). It is made in two ways:[4] chemical treatment of the surface of a special alloy plate, and cementing powdered catalyst on a metal plate surface. With the latter method, the desired property of catalyst is easily obtained, but it is necessary that the catalyst powder should not come off the metal.

Hitachi Ltd. (Section 4.3) and Mitsubishi Heavy Industries (Section 4.6) have conducted tests with plate catalysts that they have produced. The plate catalysts may be best suited for plants for which a moderate NO_x removal efficiency of 50-70 percent is sufficient.

The parallel passage reactor was originally developed by Shell and further developed for SCR by JGC. The reactor uses a small size catalyst packed in thin envelopes made of metal gauze; these envelopes are placed in parallel as described in Section 4.4.

This reactor is more efficient than the ceramic parallel plate reactor because it has a larger catalyst surface area as shown in Figure 3-14; it may cost more, however, because it requires special envelopes (Table 3-5). One of the possible problems is the deposit of a small amount of dust on the gauze. JGC has developed a sand-blast system to remove the deposit.

Tubular catalysts have been tested by several companies, including Kawasaki Heavy Industries and Mitsui Engineering. The latter commercialized the catalyst for the Chiba plant of Ukishima Petrochemical (Section 4.5). Many tubes are regularly placed so that gas flows in parallel both inside and outside of the tubes (see Figure 4-42). Mitsui Engineering has found an optimum way to pack the tubes separately in which maximum efficiency is obtained at a relatively low pressure drop. At the Ukishima Petrochemical plant, tubes with 33 mm outer and 20 mm inner diameters and 1000 mm length are used. Tubes with thinner walls (for example, 20 mm outer and 14 mm inner diameters) have been produced which have better efficiency. Tubes with even smaller diameters and thinner walls should be more efficient, but may be too weak for commercial use.

The honeycomb type catalyst may be stronger than the tubular for a given wall thickness; the production of a large honeycomb catalyst is not easy, however. The largest ceramic honeycomb currently available commercially is 150 x 150 x 500 mm. A thin-wall honeycomb catalyst with small openings can be highly efficient and has been used at a commercial SCR plant constructed by Mitsubishi Heavy Industries for Fuji Oil (Section 4.6). Recently, Ishikawajima-Harima Heavy Industries started operations with honeycomb catalysts at large plants for utility boilers (see Section 4.7).

A larger size honeycomb can be made with a metallic material by activating the surface chemically. The honeycomb is easy to handle and has been used by Hitachi Zosen for pilot plant tests (Section 4.2). Since the reactive activated surface is very thin, erosion by particulates should be prevented. Among different types of honeycombs as shown in Figure 3-14, hexagonal type may be more efficient than others which tend to collect a small amount of dust at the corners of the channels. It may also have a little less strength, however. For treating flue gas from a coal-fired boiler with a full dust load, a parallel flow catalyst with fairly large openings is needed to prevent dust plugging. Therefore, a honeycomb catalyst shape is not always the best choice.

3.4 COMMERCIAL HONEYCOMB CATALYSTS

3.4.1 Introduction

Honeycomb type SCR catalysts have been produced and tested by many companies. Most of the catalysts use a ceramic material such as TiO_2 or related compounds, while the rest are made of metals. As mentioned previously, the largest size ceramic honeycomb catalyst currently available is 150 x 150 x 500 mm with a wall thickness of about 2 mm. The honeycombs are usually packed in a container measuring about 1 x 1 x 1 m. Smaller honeycombs are easier to produce but are more difficult to pack regularly.

A few companies, including Hitachi Zosen and Mitsubishi Heavy Industries, have been working on metal-based honeycomb catalysts made by activating the surface of a special alloy. By using metal, much larger catalysts (0.5 x 0.5 x 0.5 m with a thin wall about 1 mm thick) can be produced. The metal-based catalysts are much easier to handle than the smaller ceramic ones. On the other hand, the activated surface of the metal is very thin (less than 0.2 mm usually), and it is possible that the catalyst loses activity due to erosion by particulates. This is particularly true when the catalyst is used for the treatment of flue gas from a coal-fired boiler.

Further improvements are expected on the honeycomb catalysts to make them very useful for the treatment of gases with high particulate loading.

3.4.2 Honeycomb Catalysts Produced by Catalyst and Chemicals Ind. Co.

Catalyst and Chemicals Ind. Co. is one of the largest catalyst producers in Japan and has produced several kinds of honeycomb catalysts for SCR. Results of tests with one of the catalysts are shown below.

The honeycomb has a cross section of 96.6 x 96.6 mm with a length of 300 mm (see Figure 3-17). The channels are square with an opening of 6.6 mm and wall thickness of 2 mm. For the tests, 4 honeycombs in a block were placed in 6 separate layers, so that the total cross section was 193.2 x 193.2 mm and the total depth of the layers was 1800 mm. The flue gas was obtained by burning heavy oil and had the following composition:

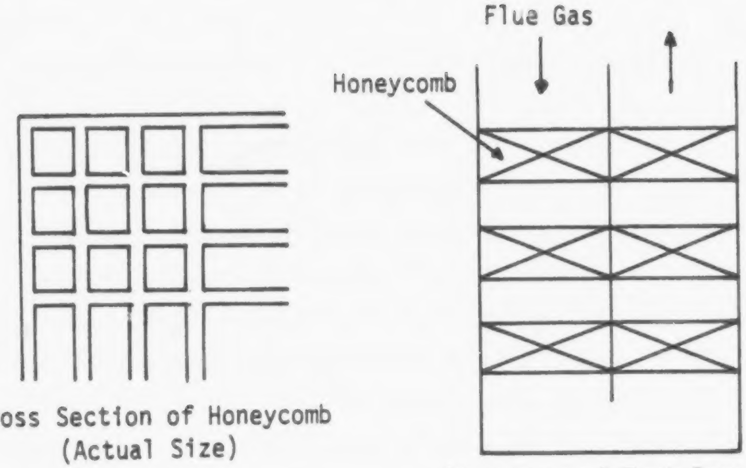
NO:	160-180 ppm	SO_2:	250-300 ppm
CO_2:	7-10 percent	O_2:	7-10 percent
H_2O:	7-9 percent	Particulates:	70 mg/Nm^3

The gas volume used for the test was 700 Nm^3/hr, and the NH_3/NO mole ratio was 1.1. The results are shown in Figures 3-18, 3-19 and 3-20. At 375°C, 90 percent NO_x removal was achieved at an SV of about 10,000 hr^{-1}. The efficiency remained unchanged at gas velocities between 5.8 and 9.5 m/sec, but was a little higher at 12.2 m/sec. Theoretically, a larger gas velocity should give more gas turbulence and larger NO_x removal efficiency. At 340°C the efficiency was slightly lower and showed no difference at gas velocities between 5.3 and 12.3 m/sec. About 90 percent NO_x removal was obtained at an SV of 8000 hr^{-1}. At 300°C, the efficiency was considerably lower. The removal efficiency was nearly 90 percent at an SV or 5500 hr^{-1}.

The catalyst may be useful in obtaining 90 percent NO_x removal for a boiler which gives gas from the economizer at 375-400°C at full load (SV = 10,000 hr^{-1}) and at 300°C or above at less than half load (SV smaller than 5000). Honeycombs (150 x 150 x 500 mm) made by Catalyst and Chemicals Ind. Co. have been used by Ishikawajima-Harima Heavy Industries for large-scale tests with utility boilers.

3.4.3 Honeycomb Catalysts Produced by NGK Insulators Ltd.

NGK Insulators Ltd., the largest ceramic insulator producer in Japan, has produced honeycomb catalysts for various uses. Figure 3-21 shows the


Flue Gas
Honeycomb

Cross Section of Honeycomb
(Actual Size)

Structure of Test Reactor

Figure 3-17. Honeycomb and reactor produced by Catalyst and Chemicals Ind. Co.

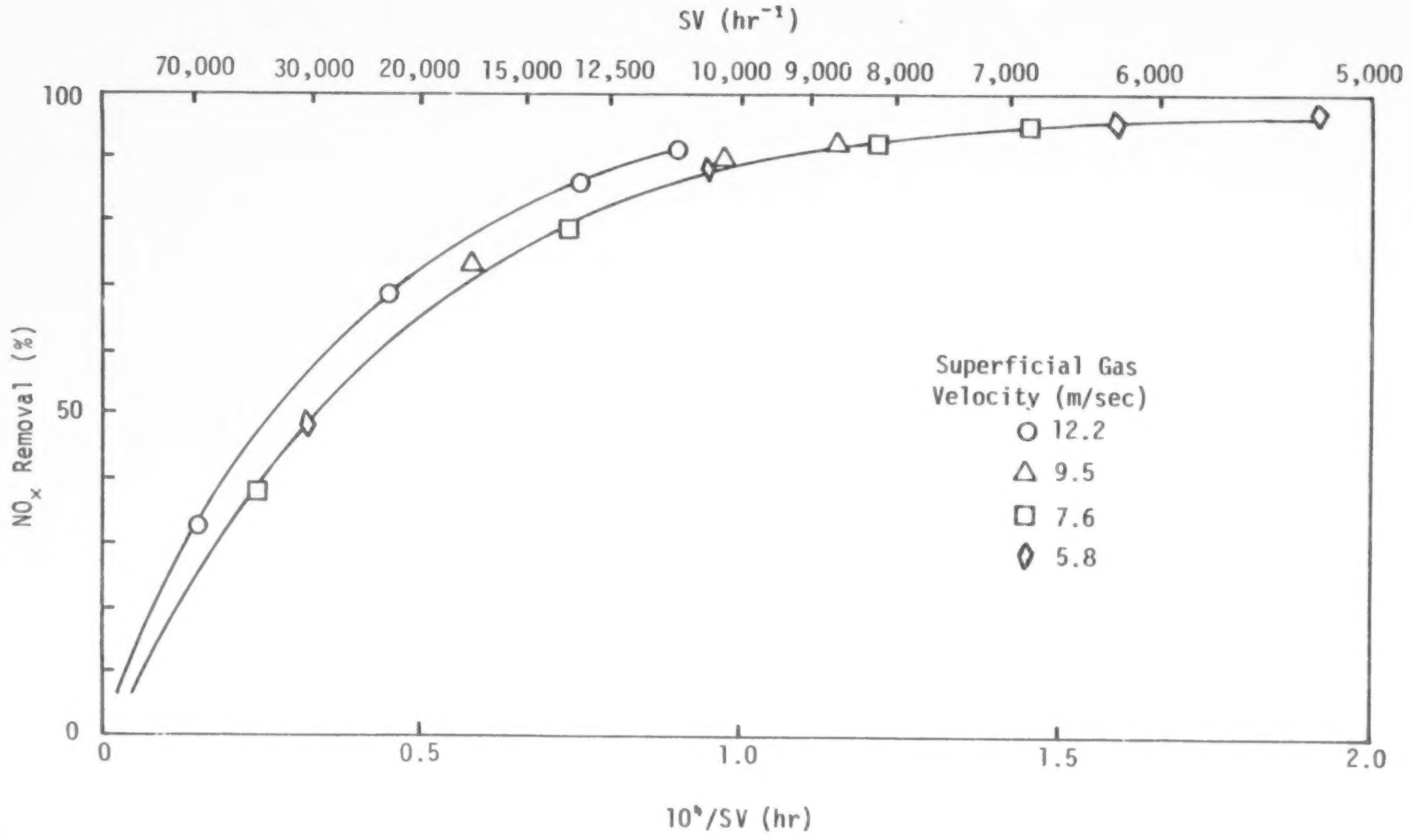


Figure 3-18. NO$_x$ removal at 375°C (NO = 160-173 ppm, NH_3/NO = 1).

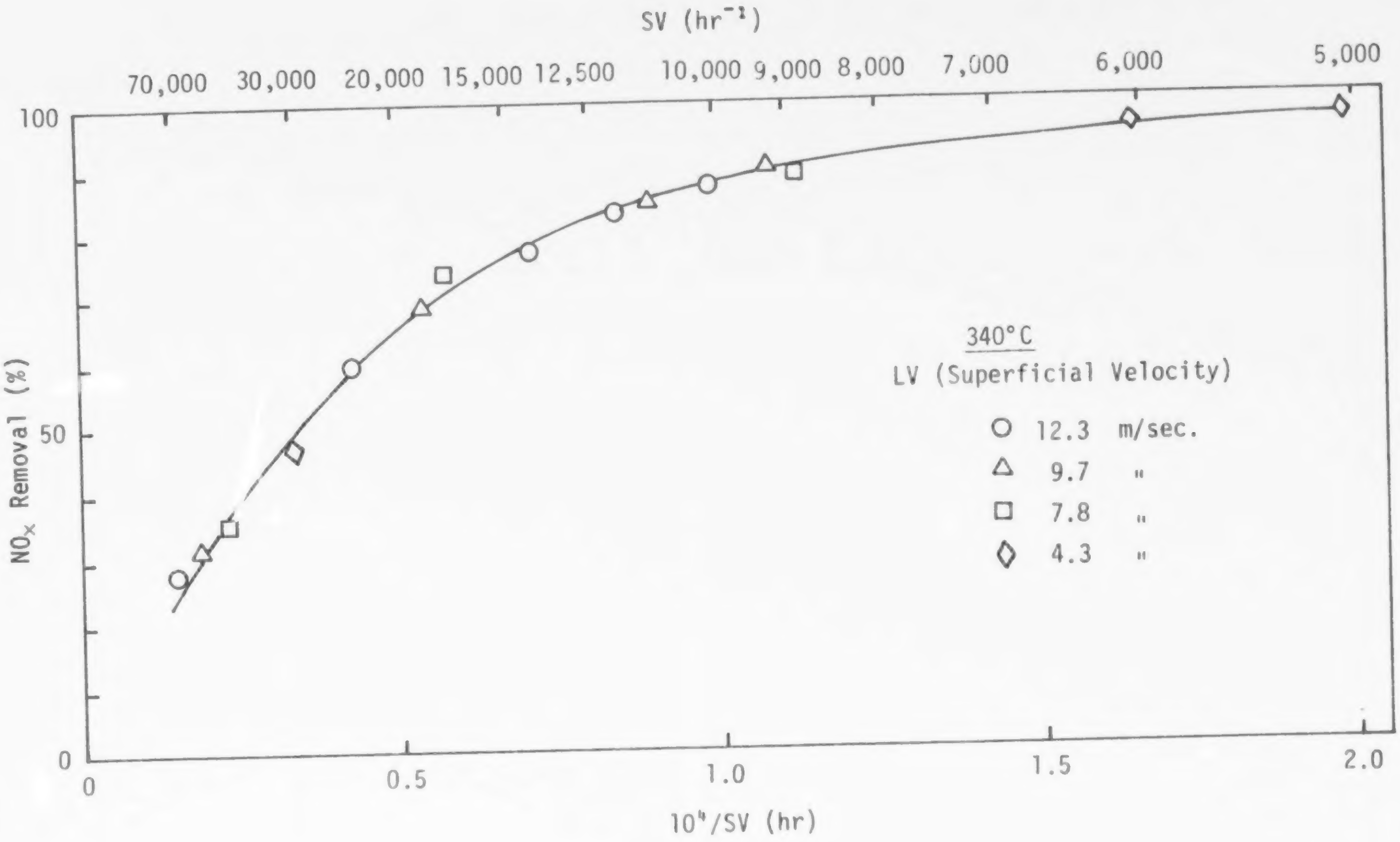


Figure 3-19. NO_x removal at 340°C (NO = 176-184 ppm, NH_3/NO = 1).

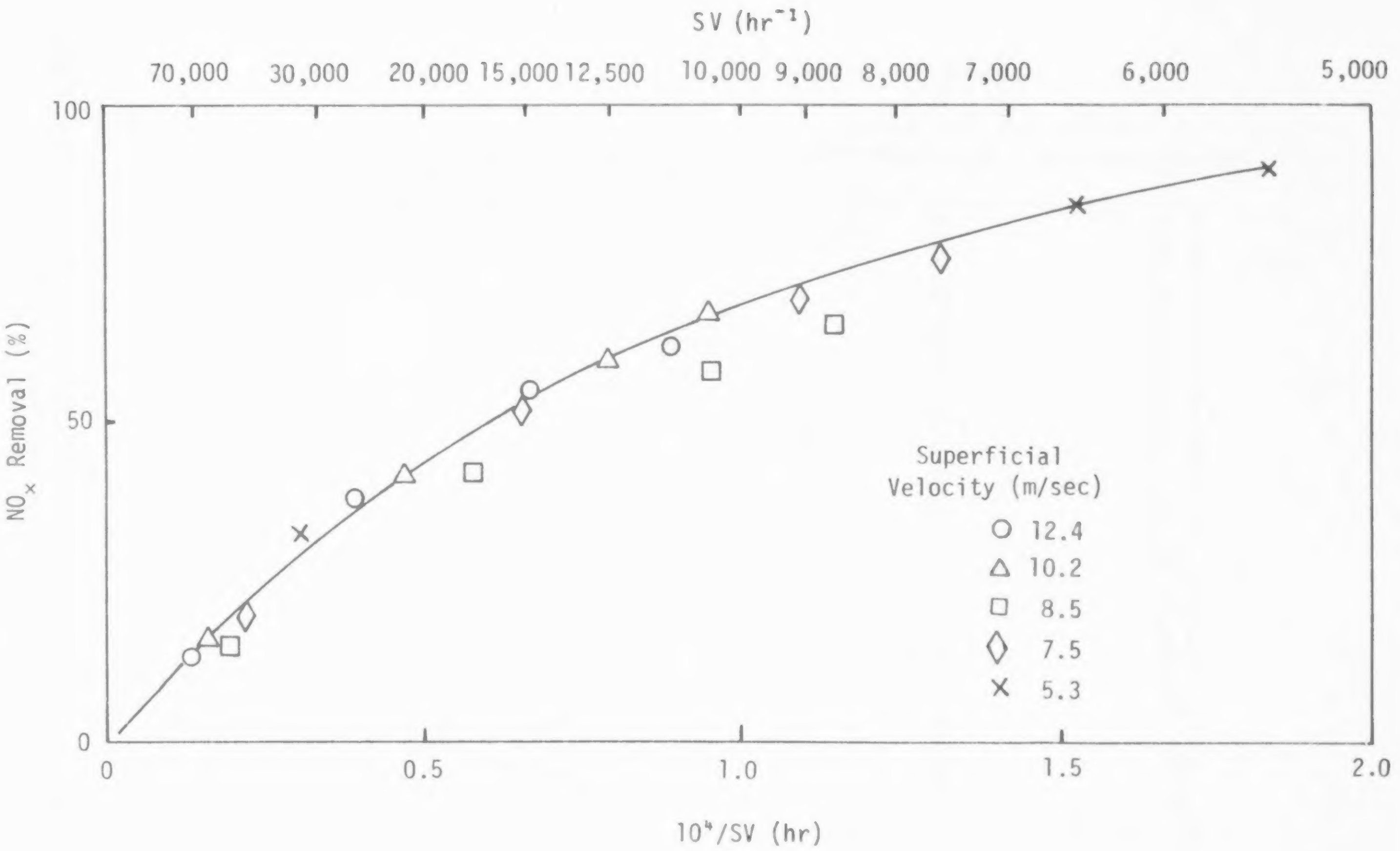
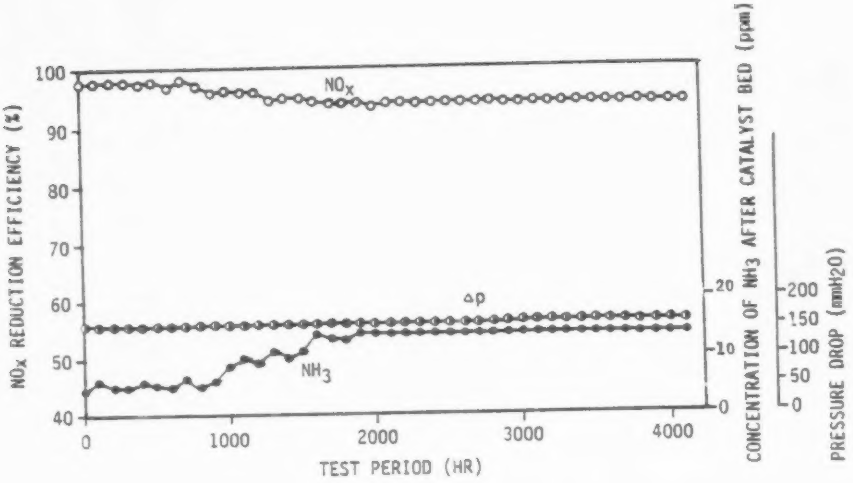


Figure 3-20. NO$_x$ removal at 300°C (NO = 163-178 ppm, NH$_3$/NO = 1).



Test condition

catalyst	NGK honeycomb-shaped catalyst
hydraulic-dia of channels	7mm
dimensions of catalyst	55mm dia. x 2000mm length
space velocity	10000 hr^{-1}
gas velocity	12.6 m/s
gas temperature	350-360°C
NH_3/NO_x (mol/mol)	1.0

Gas composition	
NO	200-250ppm
SO_2	900-1000ppm
SO_3	30ppm
O_2	4-5vol.%
CO_2	10-11vol.%
H_2O	8-10vol.%
dust	40-90mg/Nm^3
N_2	balance vol.%

Figure 3-21. Durability of NO$_x$ removal catalyst for exhaust gas of high-sulfur oil burning boiler.

results of a life test with an SCR honeycomb catalyst at 350-360°C with flue gas from an oil-fired boiler containing 900-1000 ppm of SO_2, 30 ppm of SO_3, and 40-90 mg/Nm^3 of particulates. An NH_3/NO_x mole ratio of 1.0 was used at an SV of 10,000 hr^{-1} with a gas velocity of 12.6 m/sec. The honeycomb has a diameter of 55 mm and a total length of 2000 mm.

During the first 2000 hours of the test, NO_x removal efficiency slowly dropped from 98 to 94 percent and leak ammonia (NH_3 at reactor outlet) increased from 5 to 14 ppm. Neither the efficiency nor leak ammonia changed between 2000 and 4000 hours. The pressure drop was kept constant at 160 mm H_2O during the test, indicating no particulate plugging.

A honeycomb catalyst produced by NGK has been used at Fuji Oil Co. for treating gas from an industrial boiler (Section 4.6).

3.4.4 Honeycombs Made by Other Producers

Sakai Chemical Industries has produced honeycomb catalysts for SCR, the largest being 150 x 150 x 500 mm with opening sizes ranging from 5 to 10 mm. The catalysts have been tested by Ishikawajima-Harima Heavy Industries in a large-scale test with a utility boiler. No data have been disclosed yet.

Hitachi Zosen has also produced metallic honeycombs; they will be described in Section 4.2.

There are several other companies working on honeycomb catalysts for SCR. Kobe Steel has succeeded in producing a fairly large ceramic honeycomb with a very thin wall (0.5 mm).

3.5 PROBLEMS OF AMMONIUM BISULFATE FORMATION

3.5.1 Introduction

Among the many processes for NO_x removal, selective catalytic reduction and noncatalytic reduction have been considered the most promising; both use ammonia as the reducing agent. Considerable progress has been made on the technology for these processes, and many of the problems have been almost solved. The largest problem left unsolved may be the formation of ammonium bisulfate in heat exchangers of air preheaters.

SO_3, NH_3, and H_2O present in a hot flue gas combine to form ammonium bisulfate, NH_4HSO_4, on cooling.

$$NH_{3(g)} + SO_{3(g)} + H_2O_{(g)} \rightleftarrows NH_4HSO_{4(1)} \qquad (3\text{-}15)$$

The bisulfate would form at about 210°C or below from a typical gas leaving the reactor containing about 10 ppm of both SO_3 and NH_3. A simple calculation shows that 10 ppm each of SO_3 and NH_3 in gas from a 500 MW boiler accounts for 2 tons/day of the bisulfate. The amount is sufficient to cause serious problems, such as plugging and corrosion in an air preheater or heat exchanger. Serious problems have been encountered in a few SCR facilities in Japan. The problem has not been serious in facilities which either discharge hot gas at 220°C or above without recovering much heat or burn a very low-sulfur (0.2 percent) oil; the amount of bisulfate deposit is small. For large boilers using medium- or high-sulfur fuel and requiring enough heat recovery, the bisulfate problem may be important.

It should be noted that although the formation of ammonium bisulfate causes a problem, it helps reduce SO_x emissions. Flue gas usually contains a small amount of SO_3 (considered to be present as H_2SO_4 mist), which is far more hazardous than SO_2. The SO_3 is not captured well even with FGD. With the addition of ammonia, ammonium bisulfate and sulfate are formed and can be captured fairly easily by the heat exchanger and an electrostatic precipitator.

3.5.2 Formation of SO_3

The relationship of the percent of SO_3 in total SO_x to the sulfur content of heavy oil is shown in Figure 3-22. The relationship of SO_3 and O_2 concentrations in flue gas from the combustion of heavy oil is shown in Figure 3-23. Those figures indicate that the percent of SO_3 in SO_x increases with the O_2/SO_x ratio of the gas. Therefore, low-oxygen combustion to reduce NO_x also helps to reduce SO_3. The use of less oxygen, however, tends to increase the particulate content; as Figure 3-24 shows, particulates increase as SO_3 decreases. Usually 1.5-2.5 percent of total SO_x is present as SO_3 in flue gas from a high-sulfur oil and about 3 percent in gas from a low-sulfur oil under good combustion conditions. It is said that SO_3 concentration in gas from coal is lower than that in gas from heavy oil because the former gas contains less vanadium which acts as a catalyst in the reaction forming SO_3 and moreover, it contains much fly ash which absorbs SO_3 to a considerable extent.

It should also be noted that the catalyst for selective catalytic reduction of NO_x tends to oxidize a small portion of SO_2 to SO_3. The oxidation ratio differs with the catalyst composition, temperature, and SO_2, O_2 and NH_3 concentrations. Usually the oxidation ratio is below 2 percent but a considerable amount of SO_3 is formed in SO_2-rich gas.

3.5.3 Formation of Ammonium Bisulfate and Sulfate

Figure 3-25 shows the melting point of an NH_3-H_2SO_4 system. The melting point of ammonium bisulfate, NH_4HSO_4, is 147°C. The melting point is lowered by addition of a small amount of ammonium sulfate but further addition raises the melting point significantly. A mixture of the bisulfate

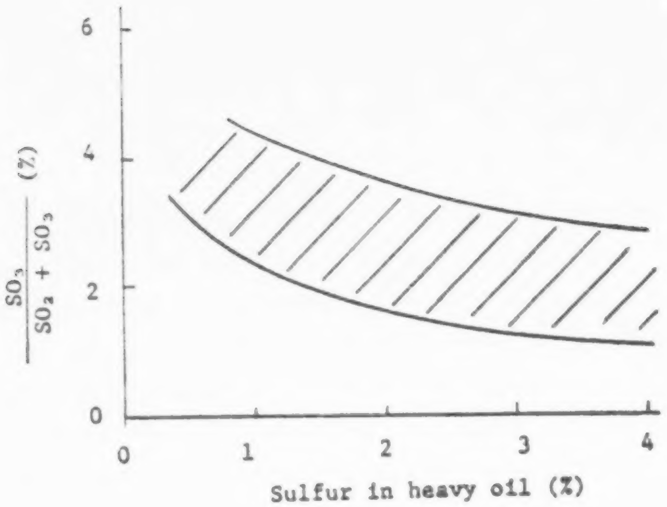


Figure 3-22. Formation ratio of SO_3 (O_2 in gas = 1-2 percent).[5]

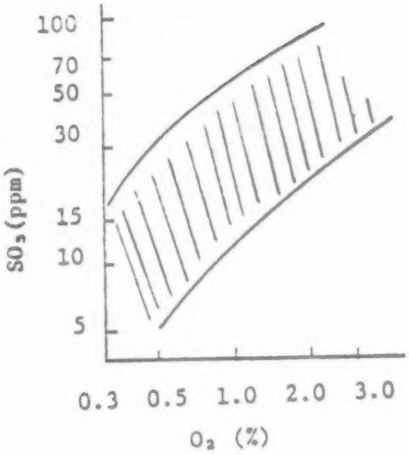


Figure 3-23. Relation of O_2 and SO_3 concentrations (heavy oil, S = 1-3 percent).[5]

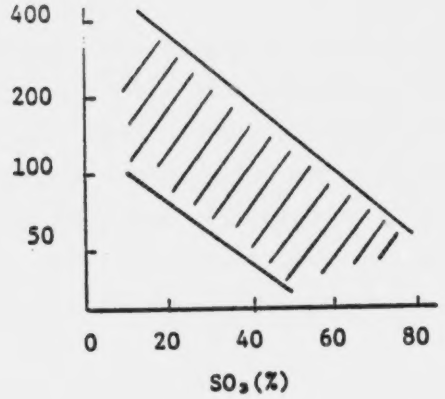


Figure 3-24. Relationship of SO_3 concentration to particulate content (heavy oil, S = 1-3 percent; O_2 in gas = 0.3-3 percent).[5]

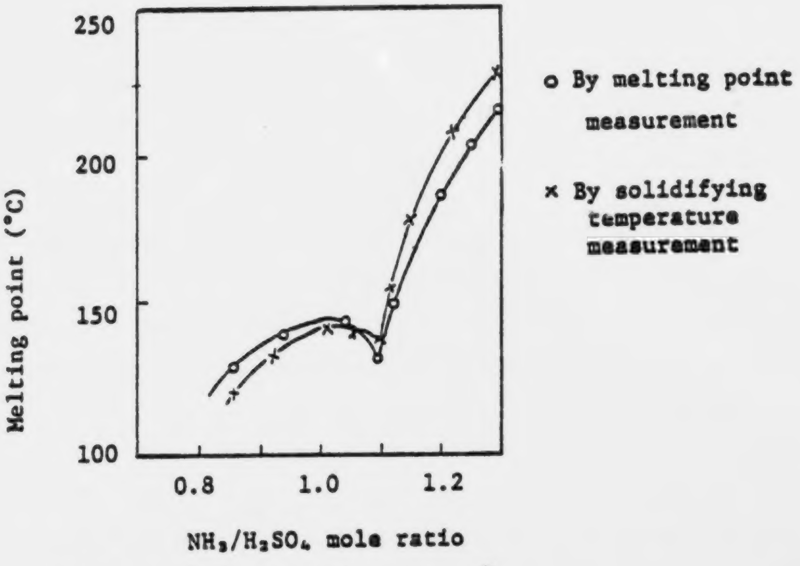


Figure 3-25. NH_3-H_2SO_4 system.[7]

and sulfuric acid has a lower melting point, is very acidic and is highly corrosive.

The formation temperatures of liquid ammonium bisulfate from the gaseous phase are shown in Figures 3-26 and 3-27. The figures indicate that the bisulfate liquid forms at about 210°C from a gas containing 10 ppm each of NH_3 and SO_3, and at about 240°C from a gas containing 100 ppm each of NH_3 and SO_3, provided that a sufficient amount of water vapor is present in the gas. For a typical SCR reactor effluent containing about 10 ppm of NH_3 and 20 ppm of SO_3, the formation temperature is about 215°C.

Figure 3-26 also indicates that solid ammonium sulfate can form from liquid ammonium bisulfate and ammonia at relatively low temperatures in the presence of excessive ammonia.

Figures 3-28 and 3-29 illustrate the formation temperatures of the bisulfate and sulfate. The formation temperatures of the bisulfate agree fairly well with those shown in Figures 3-26 and 3-27, but those of ammonium sulfate are considerably higher than those indicated in Figure 3-26. For example, Figure 3-28 shows that ammonium sulfate forms at 230°C from a gas containing 10 ppm of SO_3 and 30 ppm of NH_3. This temperature might be too high, because the sulfate decomposes to bisulfate and ammonia at a high temperature according to Figure 3-26.

Jumpei Ando, the author of the present report, has found that a double salt of the sulfate and bisulfate, $(NH_4)_3H(SO_4)_2$, forms when a flue gas containing SO_3 is cooled in the presence of excessive ammonia. Studies on the formation and decomposition of the double salt should solve the above discrepancy.

Ammonium bisulfate deposits on SCR catalysts even at 300-330°C. This may be due to high concentrations of NH_3 and also SO_3 on the catalyst

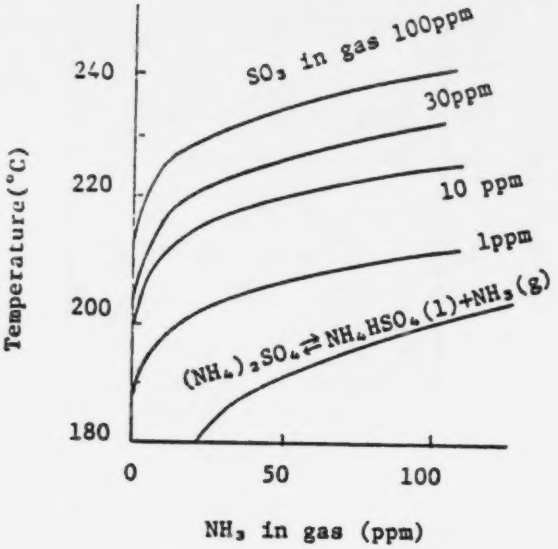


Figure 3-26. Formation temperatures of NH_4HSO_4.[6]

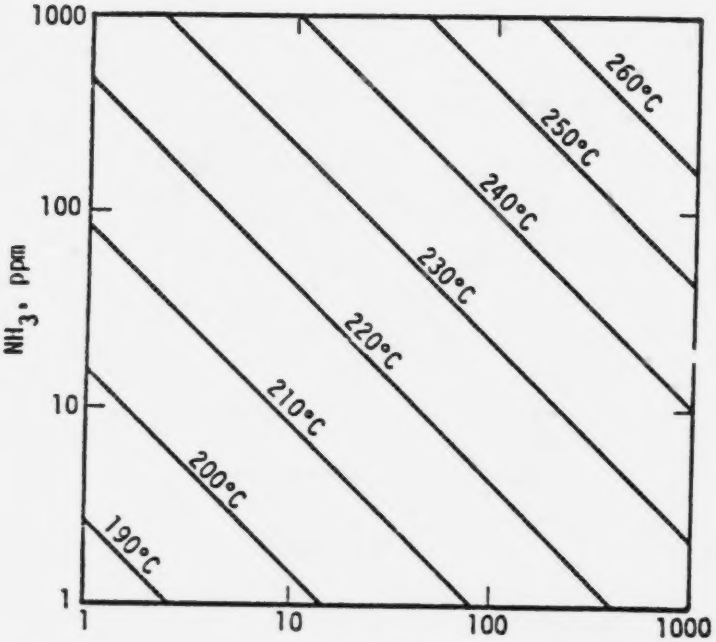


Figure 3-27. Formation temperatures of NH_4HSO_4 ($\underset{gas}{NH_3} + \underset{gas}{SO_3} + \underset{gas}{H_2O} \rightleftarrows \underset{liquid}{NH_4HSO_4}$).[6]

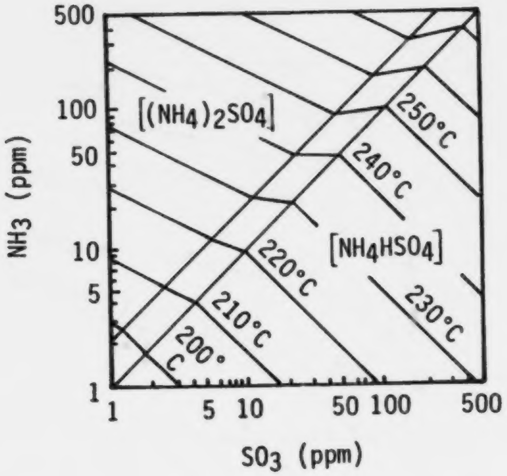


Figure 3-28. Formation temperatures of ammonium bisulfate and sulfate (1).[8]

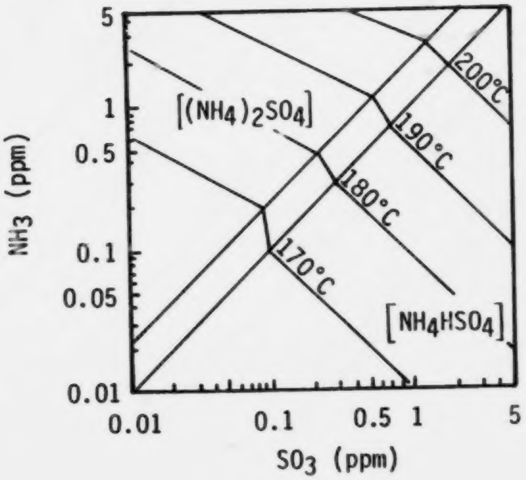


Figure 3-29. Formation temperatures of ammonium bisulfate and sulfate (2).[8]

surface, when a portion of SO_2 in the gas is oxidized to SO_3 on the catalyst surface.

3.5.4 Reaction of Ammonium Bisulfate

Ammonium bisulfate is acidic with a pH below 1, and the melt is highly corrosive. Ando has found that the bisulfate melt reacts with iron to form ferrous sulfate, which combines with ammonium bisulfate to form a newly identified double salt--$FeSO_4 \cdot NH_4HSO_4$.

$$Fe + NH_4HSO_4 + \tfrac{1}{2} O_2 = FeSO_4 + NH_3 + H_2O \qquad (3\text{-}16)$$

$$FeSO_4 + NH_4HSO_4 = FeSO_4 \cdot NH_4HSO_4 \qquad (3\text{-}17)$$

$$Fe + H_2SO_4 + \tfrac{1}{2} O_2 = FeSO_4 + H_2O \qquad (3\text{-}18)$$

Corrosion of the material occurs by reaction 3-16. In a heat exchanger or air preheater coated with corrosion-resistant material, the presence of ammonium bisulfate usually causes corrosion to some extent. The ferrous salt is formed even with an enamel-coated material, possible due to the incomplete coating which may have small pinholes or minor cracks.

It is likely that a mixture of ammonium bisulfate and sulfuric acid forms from a gas rich in SO_3 and lean in NH_3. This mixture has a low melting point (Figure 3-25) and may be even more corrosive than the bisulfate (reaction 3-18).

The melting points of ferrous sulfate and the double salt are higher than that of ammonium bisulfate. Therefore, those compounds deposit as solids above 147°C, the melting point of the bisulfate, and tend to hinder the gas flow and increase the pressure drop. From a gas rich in NH_3, ammonium sulfate and a double salt of the sulfate and bisulfate

$(NH_4)_3H(SO_4)_2$ deposits at a low temperature. Ammonium sulfate and the double salt may not be corrosive because of the higher pH and a high melting point. The pH of the ammonium sulfate solution is about 5 and of the double salt solution below 1. The deposit of the sulfates also tends to hinder the gas flow.

It seems that various deposits form under different conditions: temperature, NH_3/SO_3 ratio of inlet gas, degree of corrosion of the preheater material, and degree of reaction with fly ash. The differences in composition result in the differences in deposit properties--corrosiveness, difficulty in removing by soot blowing, etc.

Nakabayashi and Mouri[9] have found that $NH_4Al(SO_4)_2$ and $NH_4Fe(SO_4)_2$ formed in an air preheater from a coal-fired boiler used for SCR tests. The aluminum compound is formed by the reaction of NH_4HSO_4 with Al_2O_3 in fly ash from coal.

3.5.5 Deposit in Heat Exchanger and Air Preheater

Figure 3-30 shows a model of a Ljungstrom air preheater (or heat exchanger) which has rotating elements. Gas leaving the SCR reactor at 300-420°C is introduced from one side of the element and cooled to 150-200 °C, while air (or cold gas) is introduced from the other side and heated to 250-320°C.

Figure 3-31 shows temperatures of the gas and elements in a Ljungstrom heat exchanger used at a commercial SCR plant. In this plant, flue gas from an industrial boiler using high-sulfur oil is first treated by wet process FGD. The gas is then introduced into the Ljungstrom heat exchanger where it is heated from 55 to 310°C, while the gas leaving the SCR reactor at 410 °C is cooled to 170°C. After FGD, the gas contains about 150 ppm of NO_x and 150 ppm of SO_x (20-30 ppm of SO_3); the gas leaving the reactor contains 10-20 ppm of NH_3 with about 20 ppm of NO_x and 150 ppm of SO_x.

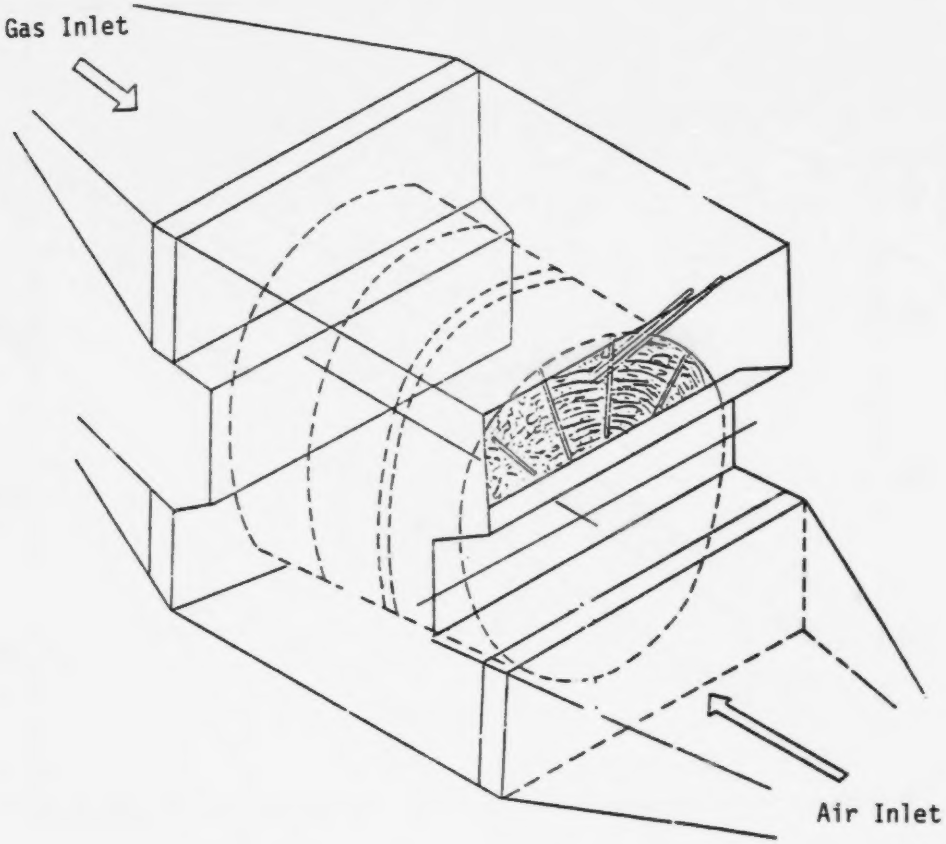

Gas Inlet
Air Inlet

Figure 3-30. Schematic of Ljungstrom type air preheater.

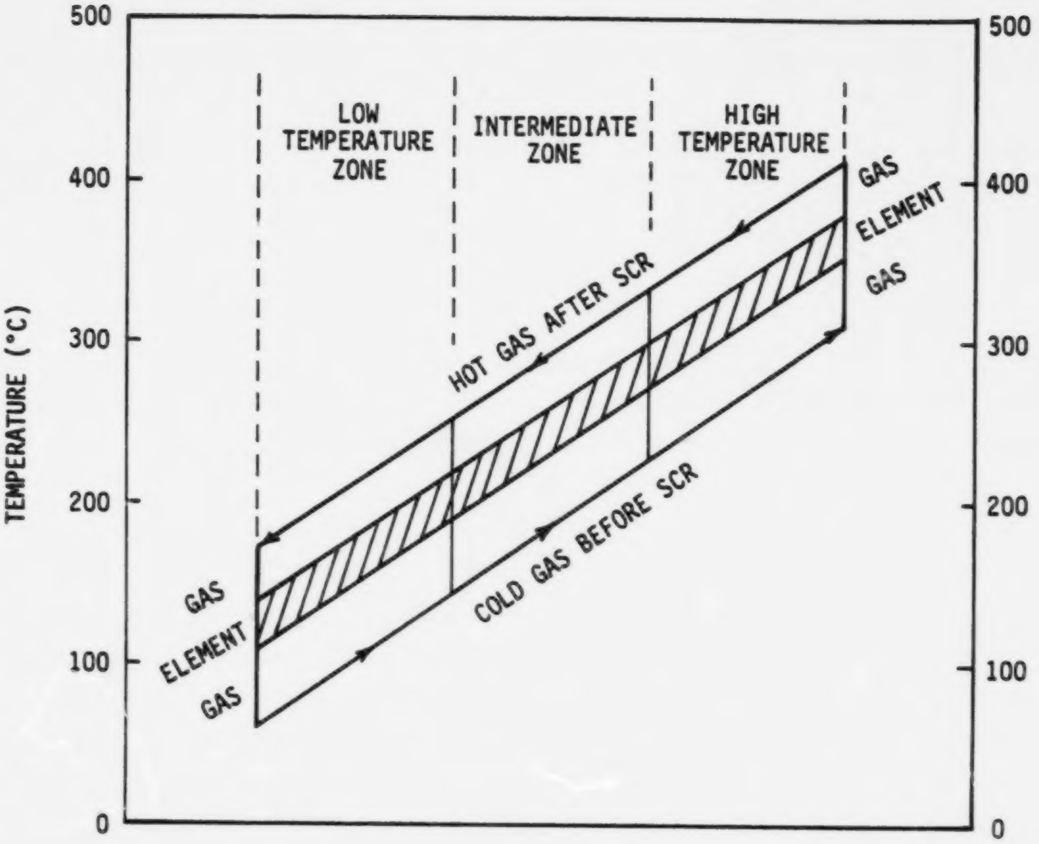


Figure 3-31. Temperatures of gas and heating elements in a commercial Ljungstrom heat exchanger.

Deposits, mainly $FeSO_4 \cdot NH_4HSO_4$ with some carbon dust, formed on the elements below 210°C and resulted in an increase in gas pressure drop. (Figure 3-32 is a photograph of a Ljungstrom air preheater before and after plugging.) Although soot blowing has reduced the deposits, the heat exchanger has required a water wash every few months. The water wash promotes corrosion because the wash liquor is acidic with a pH of about 1.

Electric Power Development Co. (EPDC) conducted tests on the deposits in an air preheater using flue gases from a coal-fired boiler containing 1400 ppm of SO_x and 300 ppm of NO_x; the flue gases had either a full particulate load or a slight particulate load after passing through a hot electrostatic precipitator. The gases (9000 Nm^3/hr) at 280-300°C were passed through a Ljungstrom type air preheater to cool to 140°C, while air at 10-40°C was heated to 260-270°C. Ammonia was injected into the gases at concentrations of either 20 ppm or 50 ppm.

The results of tests on flue gas with a full particulate load are shown in Figure 3-33.[9] Ammonia at a concentration of 20 ppm was injected for the first 480 hours and then at 50 ppm for 3240 hours (a total of 3720 hours). The pressure drop of the gas, which was 123 mmH_2O initially, increased appreciably with the injection of 20 ppm of NH_3. With 50 ppm of NH_3, the pressure drop increased rapidly and reached 185 mmH_2O at the end of the test. Deposits were formed in the low temperature and intermediate temperature zones of the heating elements.

After particulate removal in the flue gas by a hot electrostatic precipitator, the deposits formed much more rapidly, resulting in a remarkable increase in pressure drop. This shows that the fly ash of coal has a cleaning effect.

EPDC has made further tests with low particulate gas and has succeeded in reducing the deposit considerably. EPCD presumes that with high

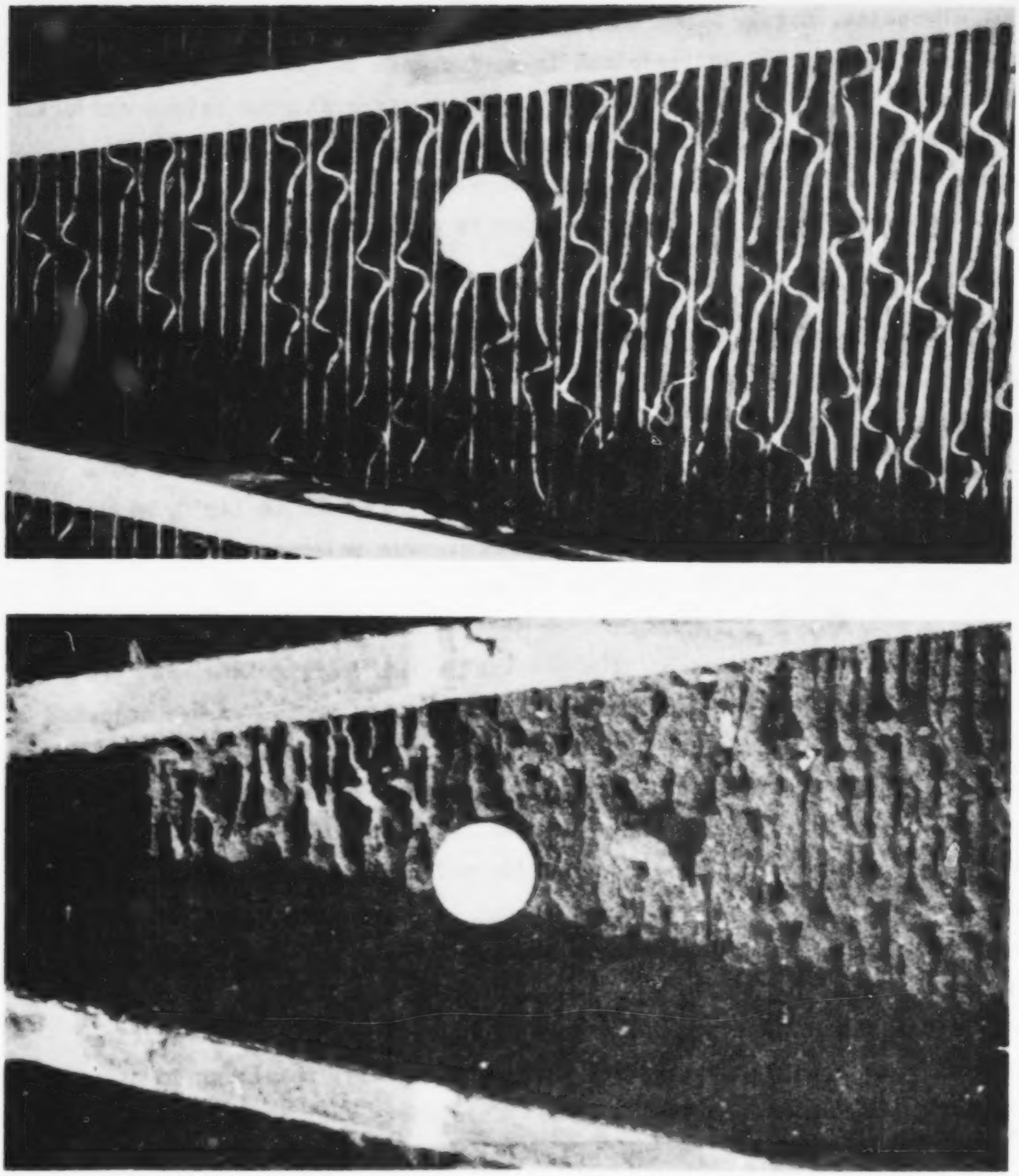


Figure 3-32. Photographs of Ljungstrom air preheater element.*

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*Above: Before plugging.
Below: After plugging by bisulfate, sulfate, and dust.
(A coin 21 mm in diameter has been inserted for size comparison.)

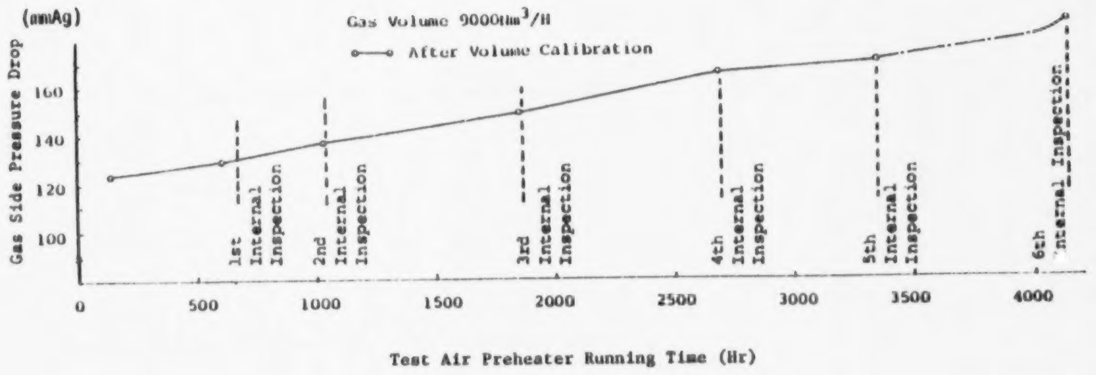

Figure 3-33. Results of tests on flue gas with a full dust load.

particulate gas the deposit may be reduced sufficiently to allow plant operation.

Figure 3-34 presents an example of a multitube type air preheater used for SCR. Air passes down the outside of the tubes, while hot gas leaving an SCR reactor goes up inside the tubes. The hot gas is at a temperature of about 370°C and contains 1500 ppm of SO_x (possibly 40-50 ppm of SO_3) and about 5 ppm of NH_3. The tube surface temperatures are between those of the hot gas and the air as shown in the figure. It has been found that a deposit forms inside the tube below 190°C.

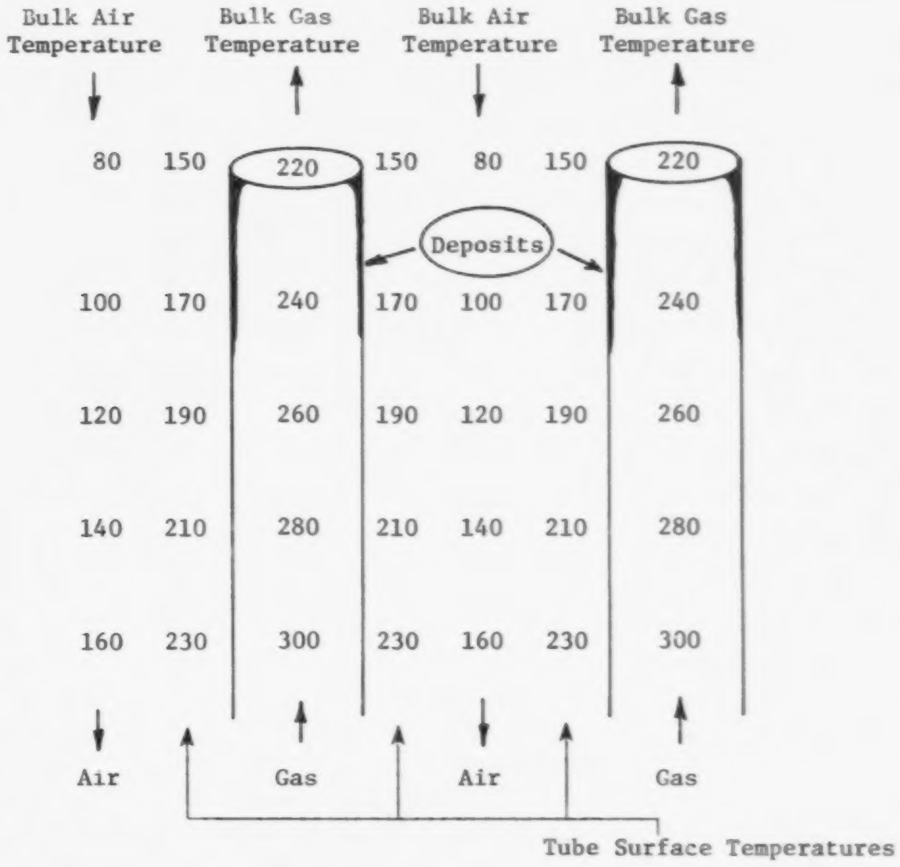
Bulk Air Temperature
Bulk Gas Temperature
Bulk Air Temperature
Bulk Gas Temperature
80 150 220 150 80 150 220
Deposits
100 170 240 170 100 170 240
120 190 260 190 120 190 260
140 210 280 210 140 210 280
160 230 300 230 160 230 300
Air
Gas
Air
Gas
Tube Surface Temperatures

Figure 3-34. Deposits in air preheater tubes (numbers show temperatures of gas, air and tube).

The amounts of deposit in the tubes are small and do not appreciably increase the pressure drop, presumably for the following reasons:

- Ammonia in the gas is kept at a low concentration.

- The gas velocity in the tubes is about 10 m/sec, in comparison with 2-3 m/sec in the Ljungstrom type heat exchanger.

- The outlet gas temperature is 200°C, as compared with 165°C for the Ljungstrom heat exchanger. The lowest temperature of the tube is 150°C, while the Ljungstrom element temperature is 110°C.

It is possible that when the gas is further cooled for better heat recovery, the amount of the deposit increases considerably. It is also likely that the liquid phase formed in the tube from a gas containing less ammonia is highly acidic (a mixture of ammonium bisulfate and sulfuric acid) and is very corrosive.

There is a possible way to prevent deposits in such a tube type air preheater. When the tubes are placed vertically as shown in Figure 3-34 and the hot gas containing SO_x and NH_3 is passed downward, ammonium bisulfate liquid will form in the tube. This liquid will drop off because the lowest temperature of the tube is 150°C, a little above the melting point. In this case, however, ferrous sulfate or the double salt may deposit if the tube material corrodes.

3.5.6 Corrosion Tests

Hitachi Zosen performed corrosion tests with the commercial Ljungstrom type heat exchanger for SCR, on 5 materials: SS-41, SS-41 coated with polyimide resin, S-ten, SUS 316, and SUS 316 JIL. Test pieces of the materials, 120 x 50 x 3 mm, were placed at 6 different points in the Ljungstrom and exposed to gas for 95 days. Since considerable deposits formed on the pieces, they were washed with an acidic solution and then weighed. The results are summarized in Table 3-6.

The corrosion rate was larger with the samples placed in colder positions due to larger amounts of acidic deposits. SUS 316 and SUS 316 JIL were fairly resistant to the corrosion. It may be difficult, however, to manufacture intricate structures of the air preheater elements with these materials. The resin-coated material showed a relatively small corrosion rate at 58-59°C, but the rate was much higher above 100°C because a portion of the resin tended to come off at the higher temperature.

Sumitomo Chemical did corrosion tests with SUS 304, NAR-F, SUS 316, and mild steel. Test peices of those materials were dipped in different concentrations of NH_4HSO_4 solutions at 40°C and 80°C for 20 hours. The corrosion rates are shown in Table 3-7.

Results of corrosion tests on SUS 304 and SUS 316 with NH_4HSO_4 and H_2SO_4 are compared in Figure 3-35. The corrosion rates with NH_4HSO_4 solution at 60-90 percent concentration are about equal to that of H_2SO_4.

3.5.7 Countermeasures for the Bisulfate Problem

The ammonium bisulfate problem may be minimized by using the following countermeasures:

1) Reduction of SO_3 or NH_3 or both in the SCR reactor effluent.

2) Application of soot blowing.

3) Use of simple air preheater configurations such as tube type to increase the benefits of soot blowing.

TABLE 3-6. RESULTS OF CORROSION TESTS PERFORMED BY HITACHI ZOSEN

		Test Piece Number	Corrosion Rate (mm/year)
Stationary Parts	Cold Gas Inlet (58-59°C)	1	0.424
		2	0.012
		3	0.518
		4	0.0098
		5	0.0094
	Cold Gas Outlet (Warmed Gas) (325-333°C)	1	0.013
		2	0.032
		3	0.012
		4	0.011
		5	0.011
	Hot Gas Inlet (410°C)	1	0.0055
		2	0.021
		3	0.0037
		4	0.0102
		5	0.011
	Hot Gas Outlet (Cooled Gas) (162-165°C)	1	0.192
		2	0.186
		3	0.184
		4	0.0035
		5	0.0043
Rotating Parts (Elements)	Cold End (105-120°C)	1	0.392
		2	0.334
		3	0.390
		4	0.013
		5	0.0048
	Hot End (364-380°C)	1	0.110
		2	0.198
		3	0.127
		4	0.0096
		5	0.0051

1 - SS-42
2 - SS-41 resin coated
3 - S-ten
4 - SUS 316
5 - SUS 316 JIL

TABLE 3-7. RESULTS OF CORROSION TESTS PERFORMED BY SUMITOMO CHEMICAL

Material	Temperature °C	Corrosion Rates ($g/m^2/hr$) at Different Solution Strengths (percent) of NH_4HSO_4				
		10	30	50	60	80
Mild Steel	40	69.70	114.00	148.70	17.10	24.70
	80	282.10	333.70	330.20	339.20	41.10
SUS 304	40	2.89	9.51	18.40	11.20	13.40
	80	17.50	127.20	284.60	287.90	95.80
SUS 316	40	0.01	0.27	0.17	0.38	2.29
	80	0.42	1.19			
NAR F	40	0.00	0.01	0.31	0.49	6.06
	80	0.04	0.84			

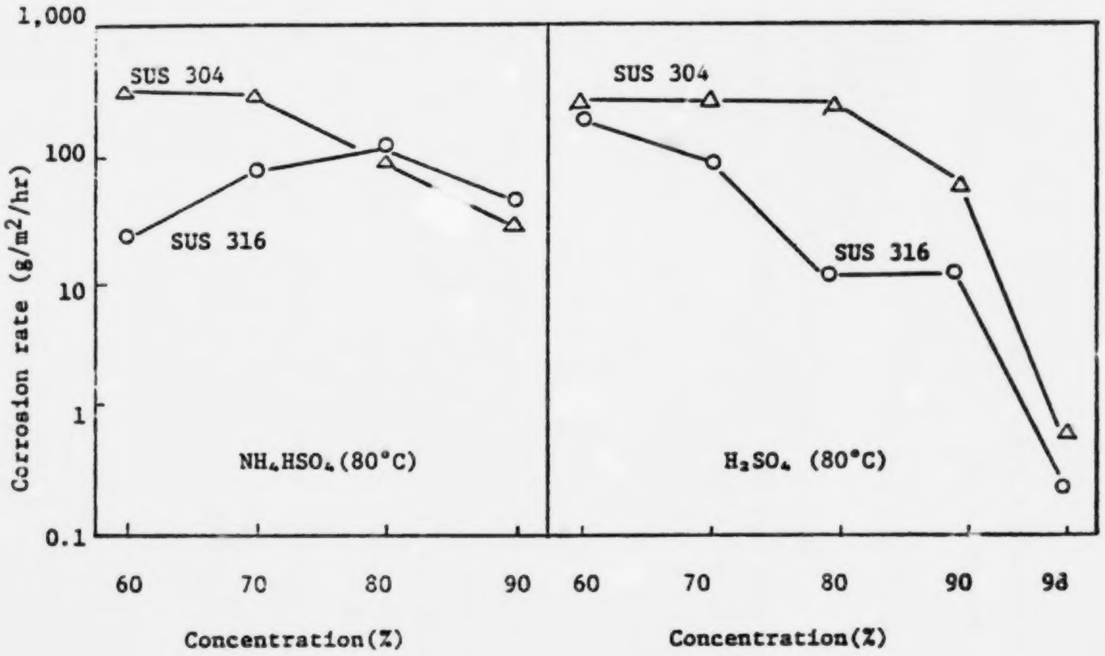

Figure 3-35. Corrosion tests on steels.[6]

4) Use of heat exchangers in which the SCR effluent passes downward at a fairly large velocity to blow down the deposits. Soot blowing may also work efficiently for such a heat exchanger.

5) Use of corrosion resistant material for low-temperature parts where the deposit forms.

When the gas contains a considerable amount of SO_3, reduction of NH_3 in the gas decreases the amount of deposit but makes it highly corrosive. The reaction product may not be easily removed by soot blowing. On the other hand, when the gas contains much more NH_3 than SO_3, ammonium sulfate and the double salt of ammonium sulfate and bisulfate form. They are less corrosive, have a high melting point, and may be relatively easily controlled by soot blowing.

For flue gas from low-sulfur fuel, the ammonium bisulfate problem can be largely solved by the above countermeasures. There is no large commercial plant yet that treats SO_x-rich gas by SCR and recovers the heat sufficiently to lower the flue gas temperature to 160°C or below. Further studies are needed for flue gas treatment from high-sulfur fuel.

It is the experience of Electric Power Development Co. (EPDC) and other companies that the ammonium bisulfate problem is less serious with flue gas from coal containing a large amount of fly ash. This may be due to two reasons:

1) When the gas is cooled, ammonium bisulfate deposits on fly ash in the gas and leaves the heat exchanger with the fly ash.

2) Even when a small amount of deposit forms on the heat exchange material, the deposit tends to be removed by erosion by fly ash.

It has also been observed that the use of a hot electrostatic precipitator to eliminate the fly ash in the gas increases the bisulfate problem. Therefore, a parallel flow type reactor should be used to minimize the bisulfate problem with particulate-rich gas.

3.6 COST OF SCR (INVESTIGATION BY ENVIRONMENT AGENCY)

3.6.1 Assumptions for Cost Estimation

The Environment Agency has investigated the costs of flue gas denitrification mainly through hearings with process developers and users partly. Three systems for new and existing oil-fired boilers were chosen for the estimation of SCR costs; they are designated as A, B and C in Figure 3-36.

System A is for a new boiler. Flue gas from a boiler economizer at 350-400°C is injected with ammonia and directly introduced into an SCR reactor without bypass. The gas leaving the reactor is passed through an air preheater for heat recovery. System A is the simplest and most economical of the three. It is used at the Chiba plant of Ukishima Chemical (see Section 4.5).

System B consists of an existing boiler that has been modified by the addition of ducts and a fan. In this system, gas that has passed through the boiler economizer is sent to an SCR reactor by a fan. Then the gas leaving the reactor is sent to an existing air preheater.

System C is for an existing boiler which cannot be modified by installing System B. In System C, the gas leaving the air preheater and electrostatic precipitator at about 150°C is passed through a gas-gas heater and a fan and is further heated by another heater to 350-400°C. The gas leaving the reactor is passed through the gas-gas heater and sent to a stack. This system is the most expensive because it requires a gas-gas heater, another heater, and much energy for the heating.

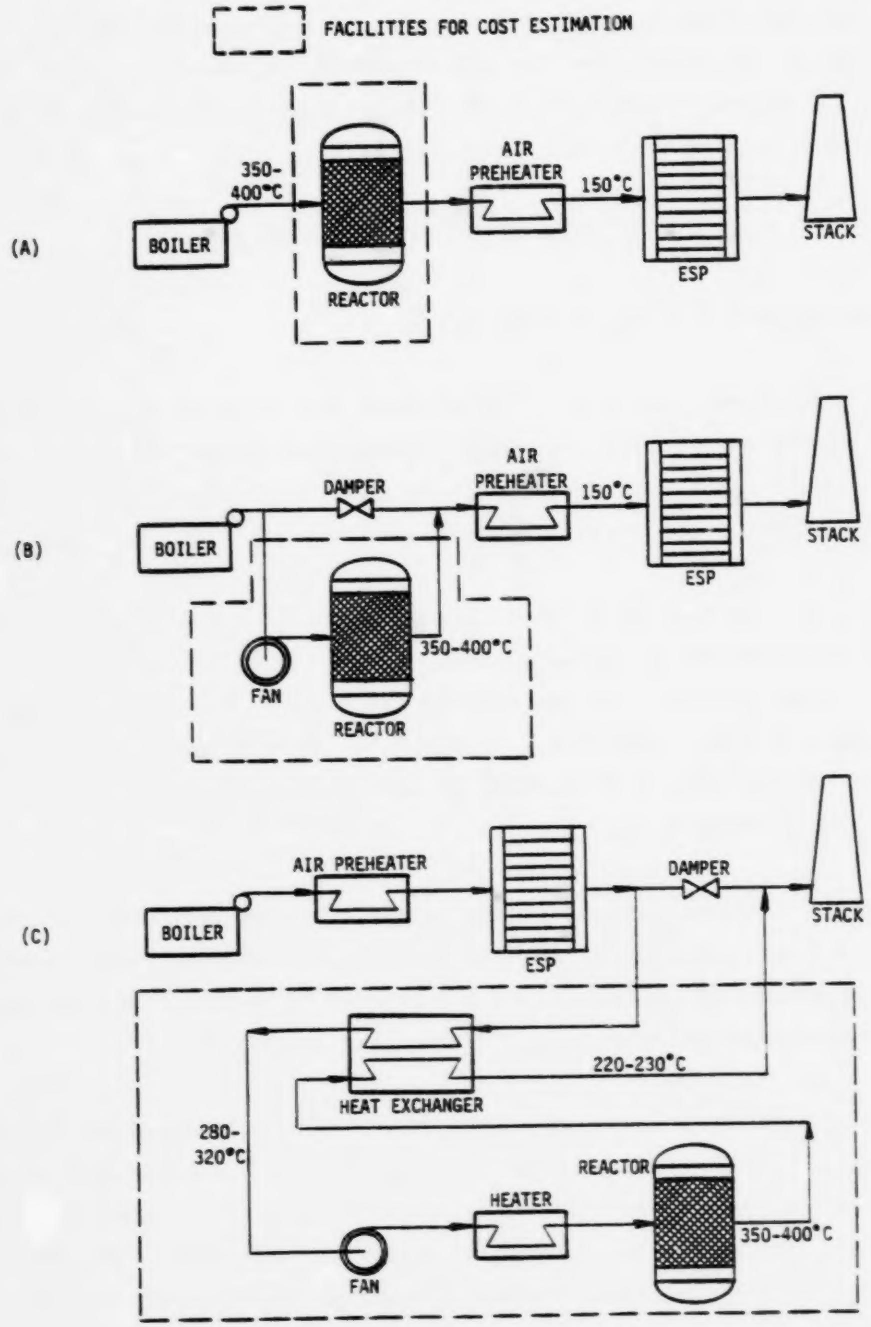
FACILITIES FOR COST ESTIMATION
(A)
BOILER
350-400°C
REACTOR
AIR PREHEATER
150°C
ESP
STACK
(B)
BOILER
DAMPER
AIR PREHEATER
150°C
ESP
STACK
FAN
REACTOR
350-400°C
(C)
BOILER
AIR PREHEATER
ESP
DAMPER
STACK
HEAT EXCHANGER
220-230°C
280-320°C
REACTOR
HEATER
FAN
350-400°C

Figure 3-36. SCR systems used in cost estimation.

The equipment cost for System A consists of costs for a reactor, ammonia storage, an ammonia vaporizer, electrical instrumentation for SCR, and an initial charge of catalyst. System B includes costs for a duct and fan in addition to the plant cost for System A. System C includes all the costs for System B plus those for a gas-gas heater and another heater.

For cost estimating purposes, the flue gas composition was assumed to be 200 ppm of NO_x, 1500 ppm of SO_x, and 200 mg/Nm^3 of particulates at 380 °C. The NO_x removal efficiency was assumed to be 80 percent.

To calculate the annual SCR cost, the following estimates were used:

Fixed Costs-- 7 years depreciation

10 percent interest/year (maintenance, 3 percent; insurance, 2 percent; and overhead, 5 percent of investment cost)

Variable costs--	Catalyst life	2 years
	Annual operation	8000 hours
	Power	12 yen/kWhr ($0.06/kWhr)
	Ammonia	80 yen/kg ($0.40/kg)
	Steam	2 yen/kg ($0.01/kg)
	Kerosene for gas heating	32 yen/kg ($0.16/kg)

3.6.2 Equipment Cost and Annual Cost

Figures 3-37 - 3-39 show equipment costs in battery limits for Systems A, B and C with different capacities ranging from 40,000 to 1,000,000 Nm^3/hr (13-330 MW equivalent). The plant costs were proposed by five vendors. One of them presented a relatively high cost, while the other four presented considerably lower costs. The high cost is close to the actual cost for plants already in operation. The lower costs may be assumed to be based on

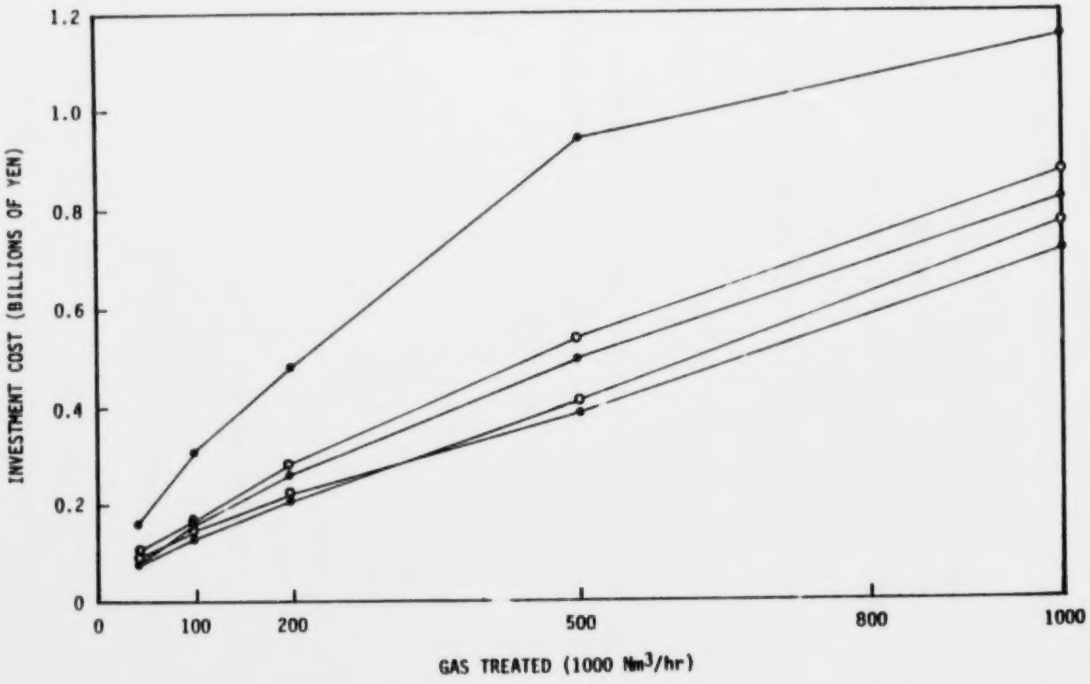

Figure 3-37. Investment cost of SCR by direct process (System A).[3]

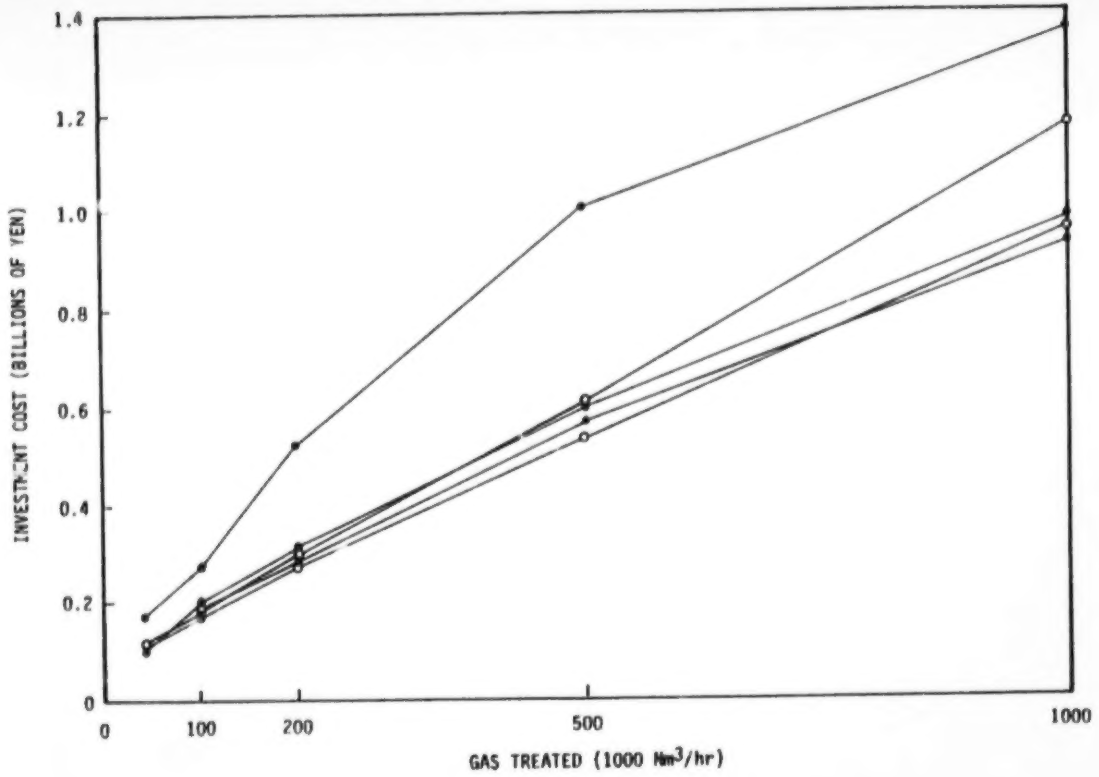

Figure 3-38. Investment cost of SCR by direct process (System B).[3]

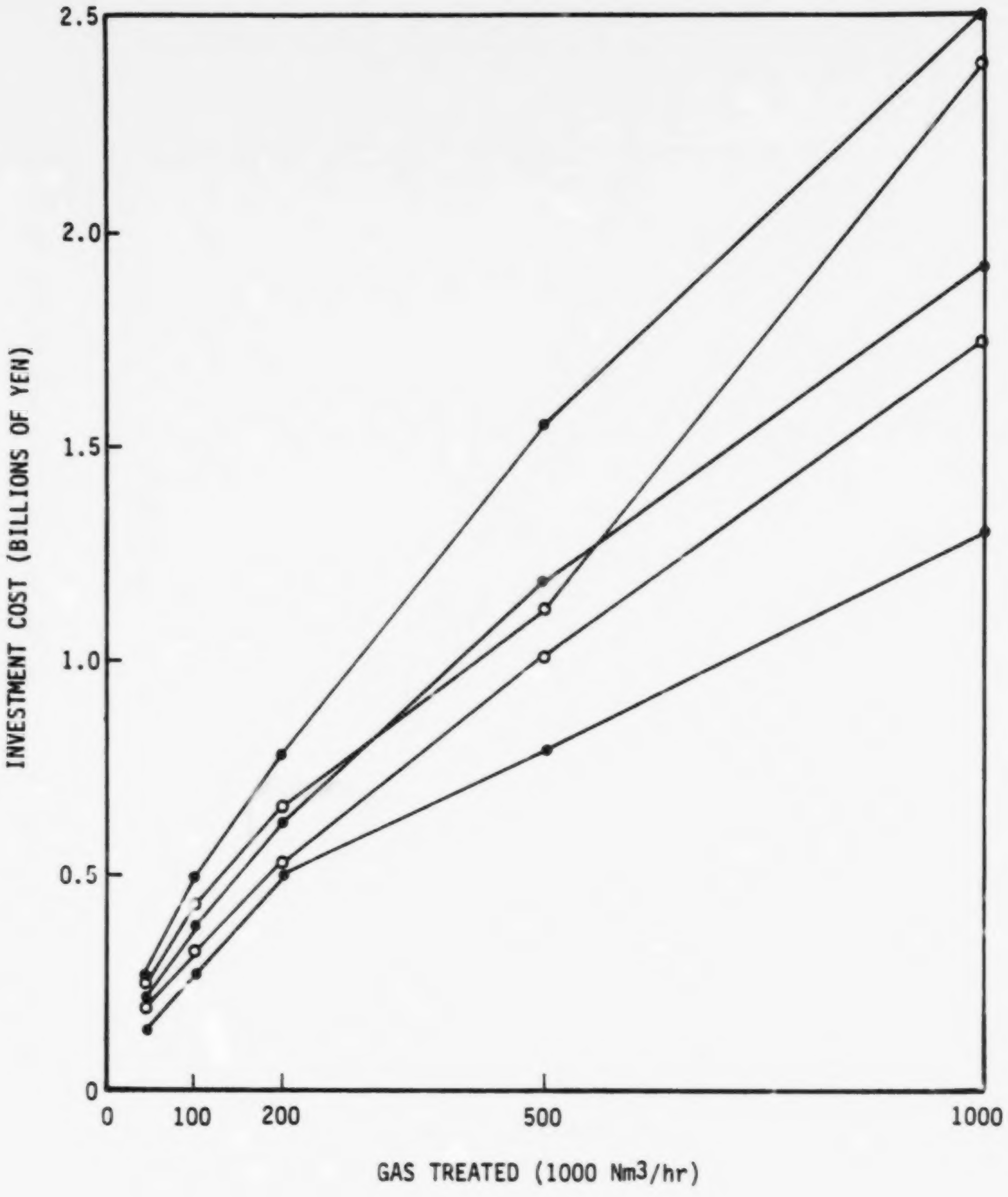

Figure 3-39. Investment cost of SCR with gas reheating and heat recovery (System C).[3]

extensive advances which permit cost reduction, but some of them could be a little optimistic. Two of the curves in Figure 3-39 show a larger inclination above 600,000 Nm^3/hr than between 200,000 and 500,000 Nm^3/hr. This is due to the use of one reactor below and two reactors above 600,000 Nm^3.

The average costs of the five vendors for the three systems are compared in Figures 3-40 and 3-41. The average cost for a 200-300 MW plant is about 2800 yen/kW ($14/kW) for System A, 3700 yen/kW ($18.50/kW) for System B, and 6300 yen/kW ($31.50/kW) for System C. The difference between System A and System B is due to the additional ducts and the fan, and that between System B and System C is due to the heat exchanger (gas-gas heater), heater and duct.

Figures 3-42 - 3-44 show annual SCR costs for the 3 systems. The costs differ considerably from vendor to vendor. Figure 3-45 shows the average of the 5 vendors' costs for the 3 processes. For a 200-300 MW size plant, the cost is about 0.3 yen/kWhr ($0.0015 kWhr) for System A, 0.4 yen/kWhr ($0.002/kWhr) for System B, and 0.7 yen/kWhr ($0.0035/kWhr) for System C. The latter cost is the highest due to the high investment cost and fuel requirement for gas heating.

3.6.3 Factors that Affect Cost

System A is simple and has the lowest cost, which is only one-fourth that for flue gas desulfurization. (FGD entails about 15,000 yen/kW in investment and 1.4 yen/kWhr in annual costs.) The cost of System C is only about half that of FGD. There are, however, several factors that may increase the cost for SCR as shown below:

1) Energy Requirement for System A - System A includes no fan. The fan for the boiler, however, needs increased capacity and energy to compensate for the pressure drop by the SCR system.

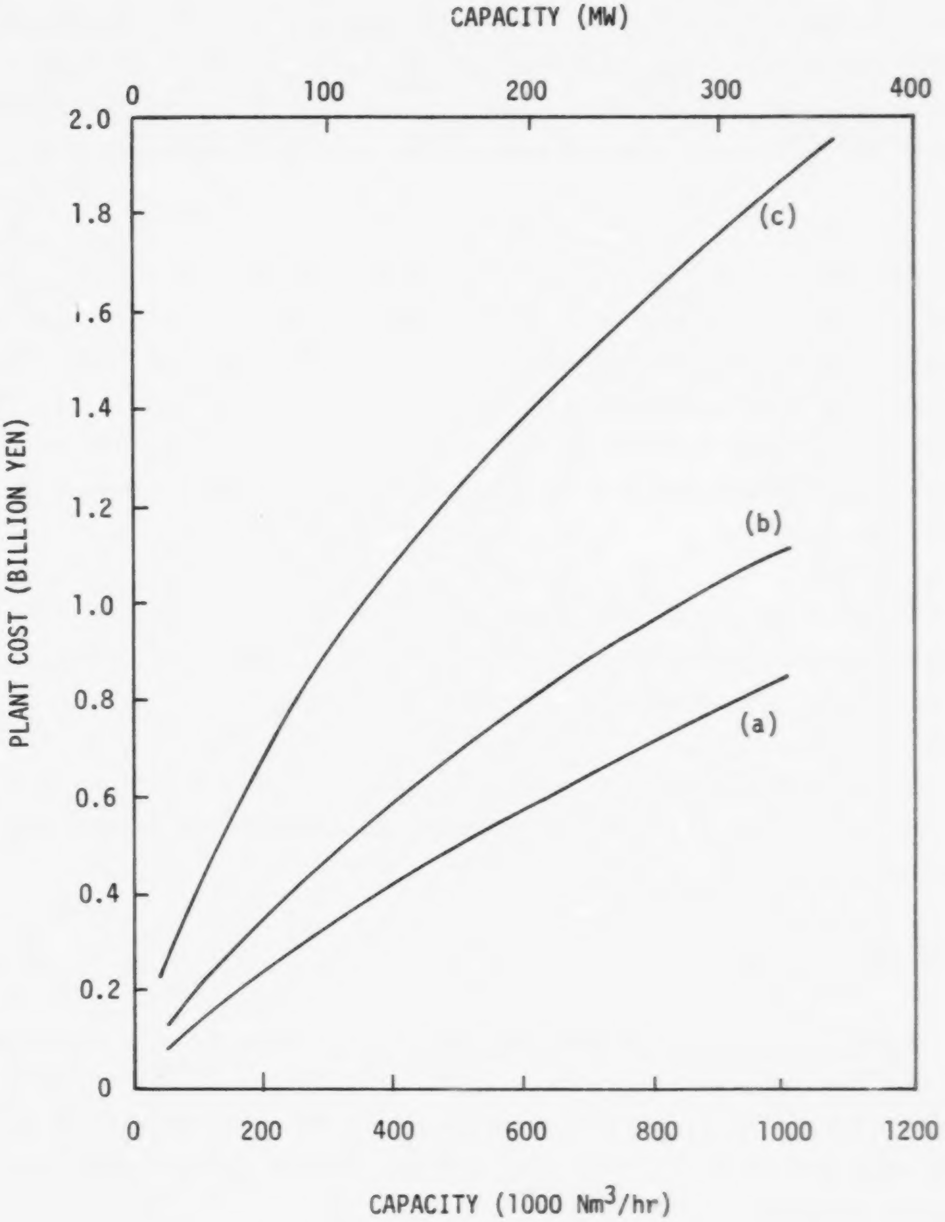

Figure 3-40. Average plant costs per capacity for Systems A, B and C.

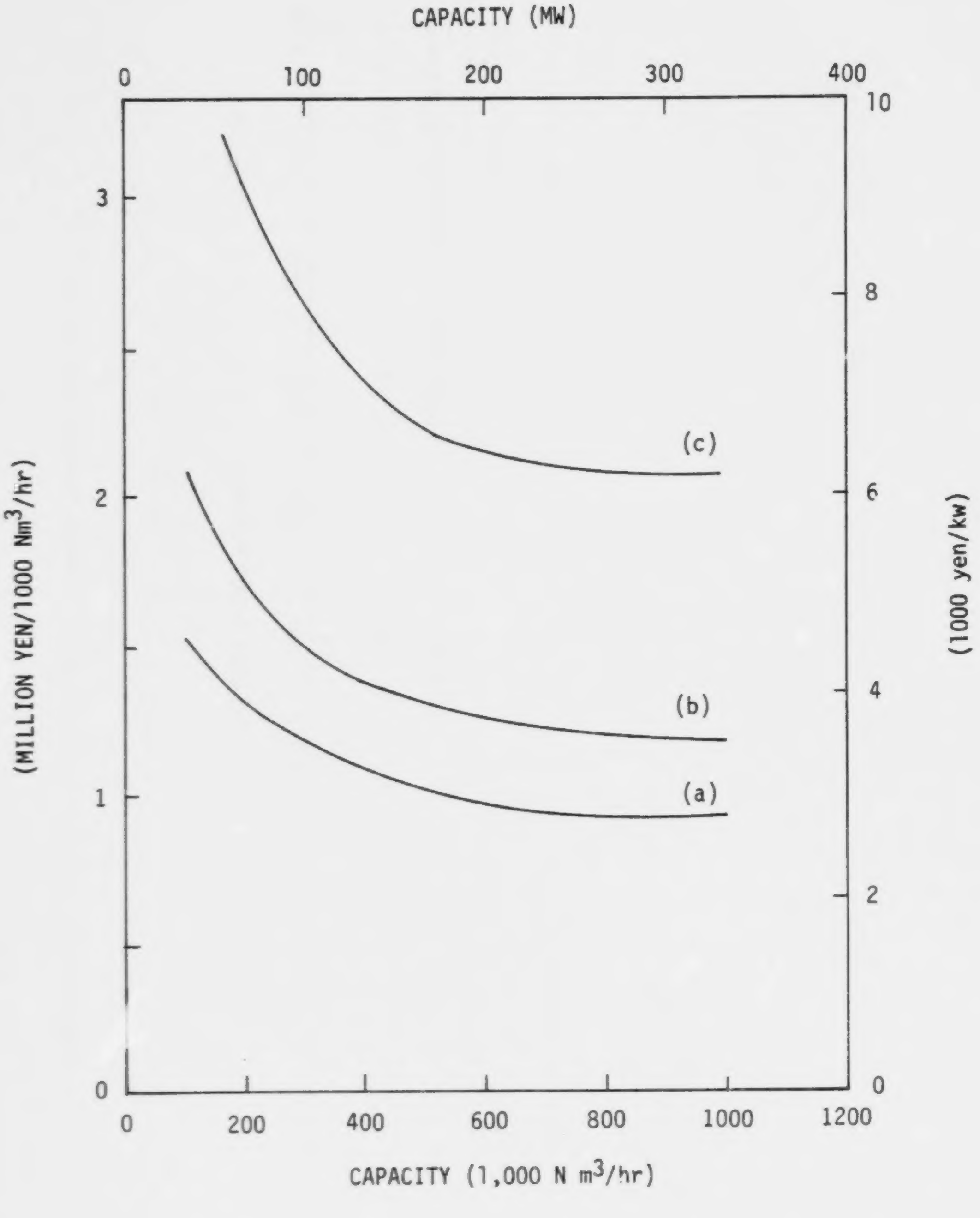

Figure 3-41. Average plant costs for Systems A, B and C.

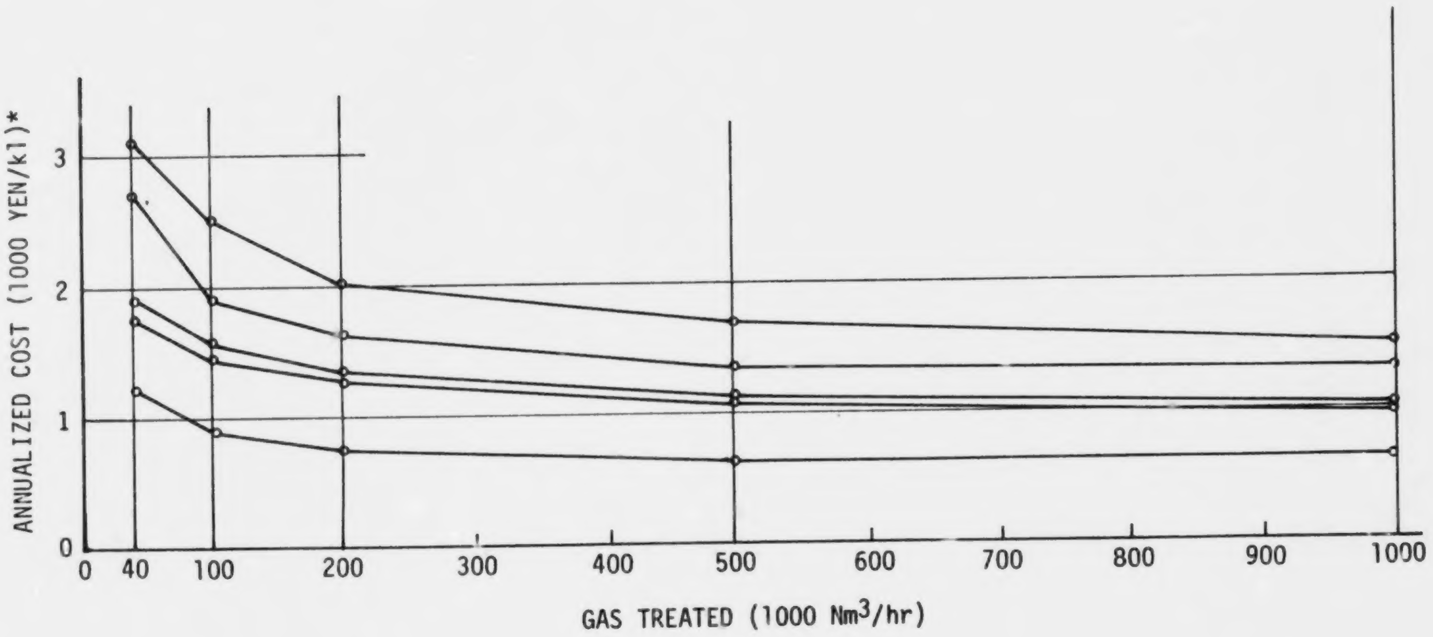

Figure 3-42. Annual cost of SCR by direct process (System A).[3]

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* Heavy oil, about 9500 kCal/1.

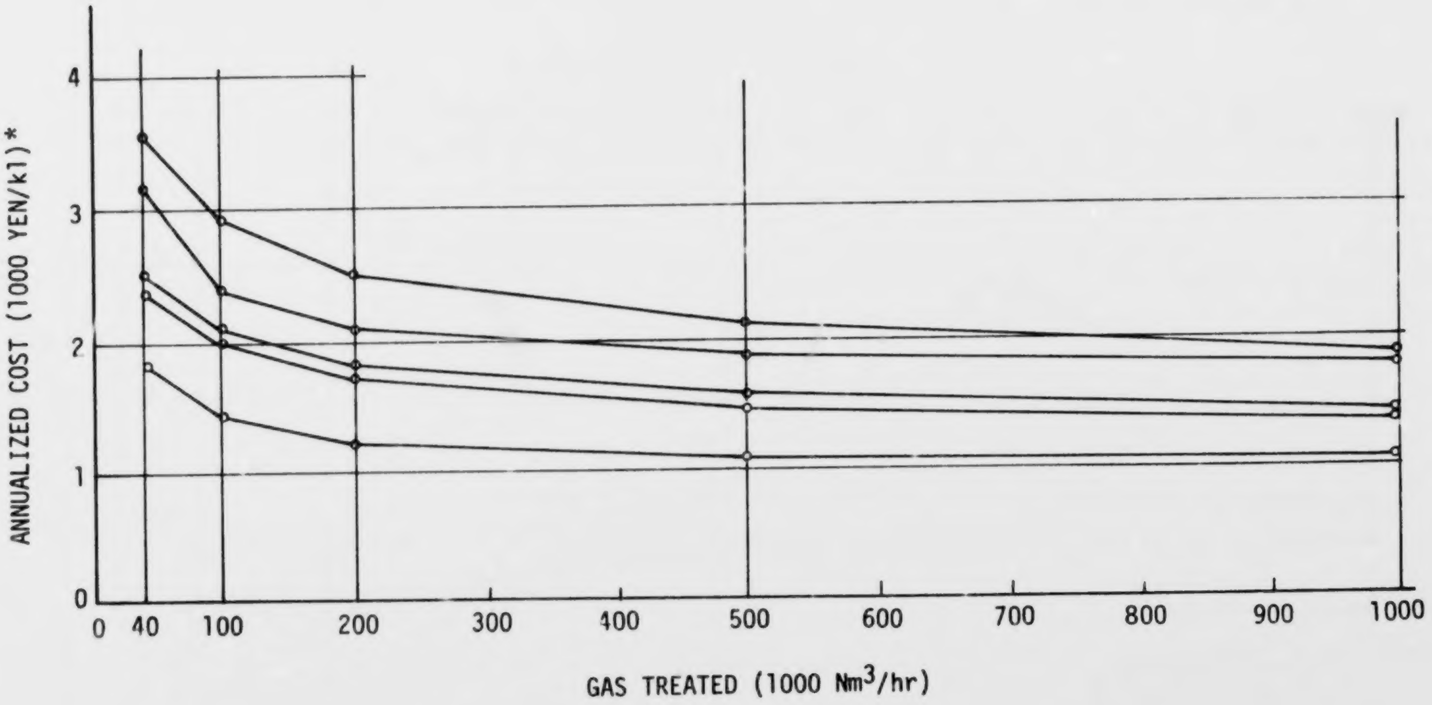

Figure 3-43. Annual cost of SCR by direct process (System B).[3]

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* Heavy oil, about 9500 kCal/l.

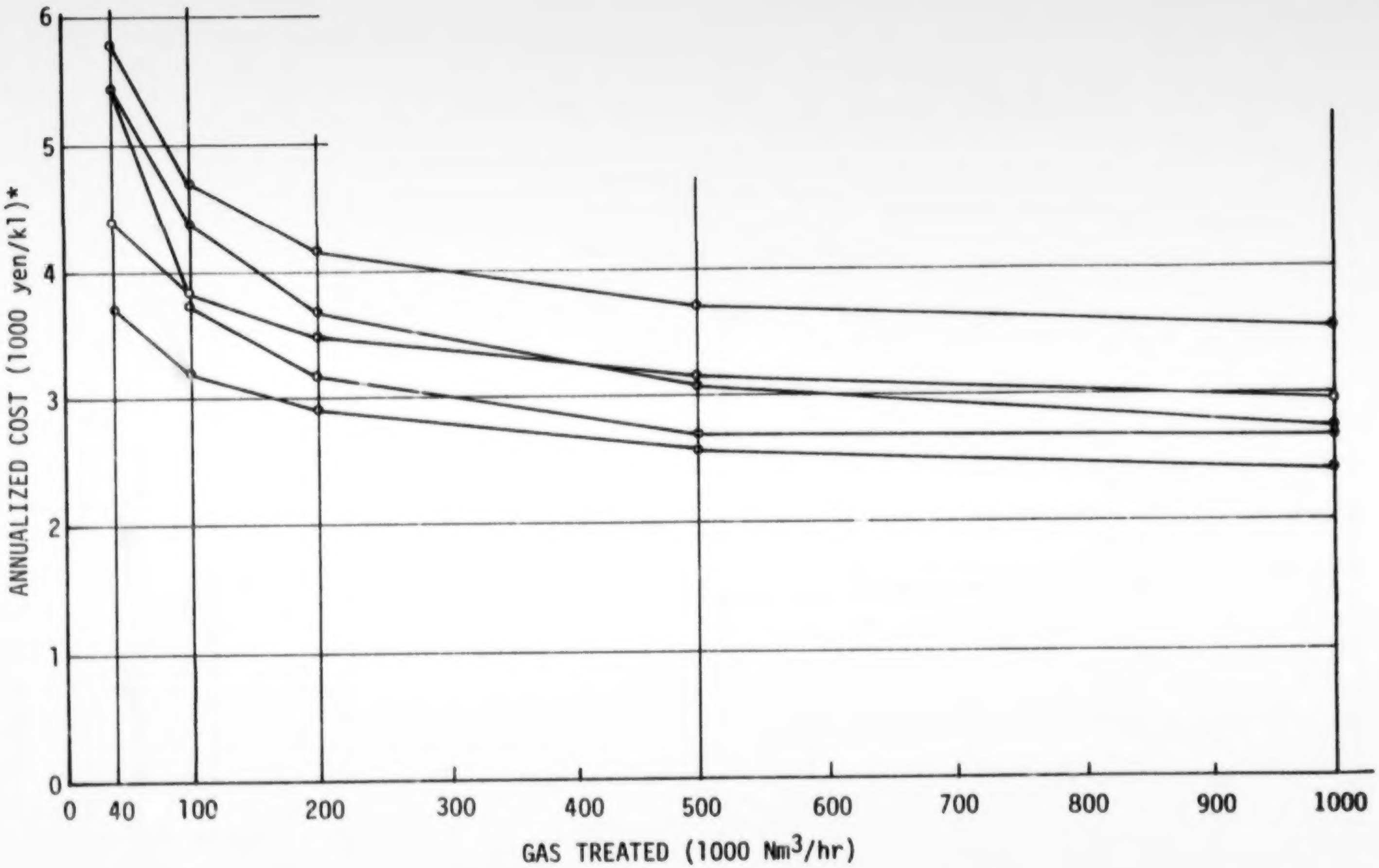

Figure 3-44. Annual cost of SCR process with gas reheating and heat recovery (System C).[3]

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* Heavy oil, about 9500 kCal/1.

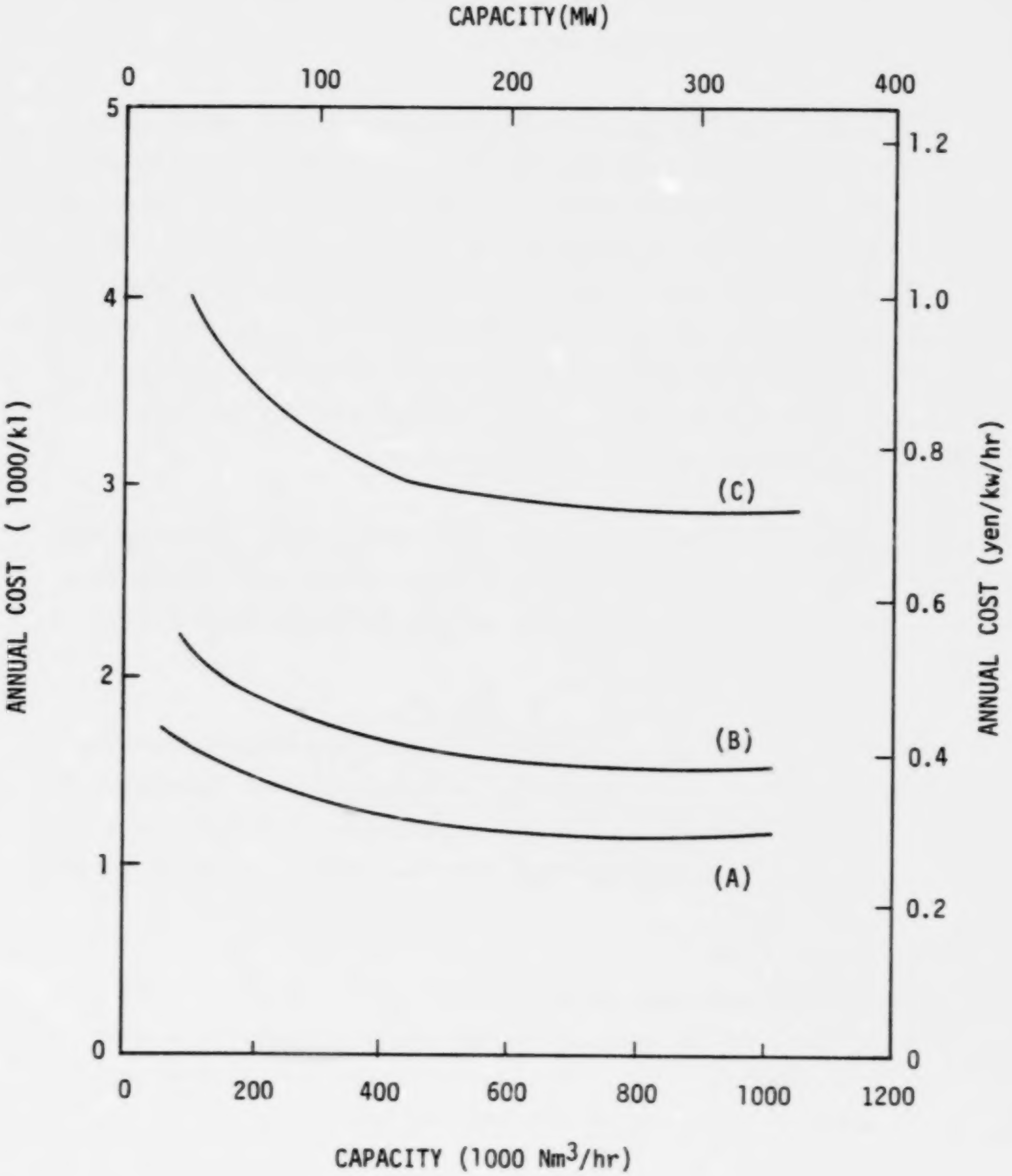

Figure 3-45. Average annual costs of SCR with Systems A, B and C.

When this cost is taken into account, the cost for System A may increase by 10-20 percent.

2) Boiler Load Fluctuation - With utility boilers which undergo a considerable load fluctuation, the economizer outlet gas temperature may occasionally drop below 300-330°C, resulting in the deposit of ammonium bisulfate on the catalyst. When a high sulfur fuel is used, it may be necessary to maintain the gas temperature above 300-330°C; this can be achieved either by installing an auxiliary burner or a bypass to mix a portion of the hot gas before it goes through the economizer with the gas after the economizer.

   Such facilities increase the investment cost. The operating costs may not increase appreciably because most of the heat required to raise the gas temperature can be recovered by the air preheater.

3) Ammonium Bisulfate Problem - The ammonium bisulfate problem described in Section 3.5 may increase the cost somewhat. The problem, however, may not be appreciable with flue gas from a coal-fired boiler because ammonium bisulfate can be removed with the ash.

4) Catalyst Life and Disposal - The catalyst life of 2 years assumed for the cost estimation may not always be achieved for dirty gas rich in SO_x, particulates and catalyst poisons. Disposal of the spent catalyst may add some cost.

5) Combination with FGD - When FGD is applied after SCR, accumulation of ammonia in the scrubber liquor and the need for ammonia removal may constitute a cost-increasing factor.

Although there are several factors that may increase SCR costs, there is also the possibility of cost cuts through further improvement of the catalyst and reactors. More complete and accurate SCR cost data will be available in the near future from the operation of many large plants for dirty gases.

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SECTION 4

SCR PROCESSES AND PLANTS

4.1 SUMITOMO CHEMICAL SCR PROCESSES

4.1.1 Introduction

In 1968 and 1972, Sumitomo Chemical, one of the largest chemical and petrochemical companies in Japan, constructed two nonselective catalytic reduction process plants for the removal of NO_x from the tail gas of nitric acid plants. Sumitomo Chemical has further developed the chemistry and technology for the selective catalytic reduction of NO_x in flue gas, tested more than one thousand catalysts, and constructed several commercial SCR units. In 1974, they completed the world's first commercial SCR unit for combustion gas treatment.

For the commercial units, Sumitomo Chemical uses granular catalysts in fixed and moving beds. The SCR units treat flue gas from industrial boilers or from heating furnaces at ammonia and methanol plants of Sumitomo Chemical and related companies.

4.1.2 Commercial Plant for Clean Gas Treatment

The first commercial SCR plant began operation in May, 1974. It treats 200,000 Nm^3/hr of clean flue gas from the burning of LPG in a reformer at the Sodegaura plant, Higashi Nihon Methanol Co. (HNM). A flowsheet of the denitrification process at the HNM plant is shown in Figure 4-1. The flue gas containing about 200 ppm NO_x (Mainly NO) at about 320°C is injected with ammonia at an NH_3/NO_x mole ratio of 1 and introduced into a reactor

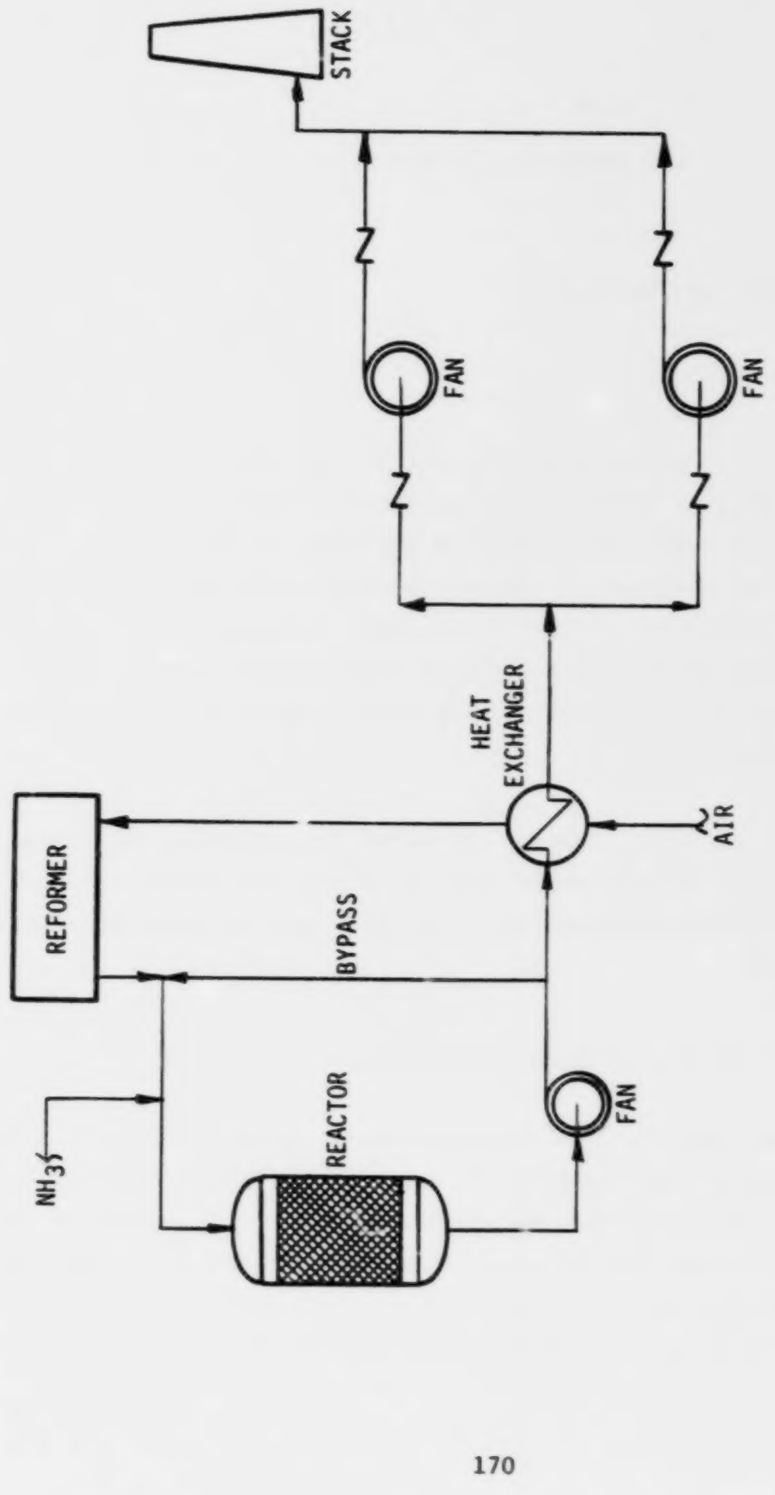

STACK
FAN
FAN
HEAT EXCHANGER
AIR
REFORMER
BYPASS
NH$_3$
REACTOR
FAN

Figure 4-1. Flowsheet of the denitrification process at the Higashi Nihon Methanol Company.

containing a base-metal catalyst. About 90 percent of the NO_x is reduced to N_2 by reaction with ammonia. The treated gas passes through a fan and heat exchanger to a stack.

The data for the standard operation of the HNM plant and two other SCR plants for clean gas treatment are shown in Table 4-1.

TABLE 4-1. DATA FOR OPERATION OF SCR PLANTS FOR CLEAN GAS

	Plant Owner		
	Higashi Nihon Methanol (HNM)	Nippon Ammonia	Sumitomo Chemical
Major Product	Methanol (800 t/day)	Ammonia (1550 t/day)	Ammonia (810 t/day)
Fuel	LPG	LPG	Off Gas
Gas for SCR (Nm^3/hr)	200,000	250,000	200,000
Inlet Gas Composition			
O_2 (percent)	7	6	5
SO_x, particulate	None	None	None
NO_x (ppm)	200	200	200
Reaction Temperature (°C)	320	320	320
Load Fluctuation (percent)	60-100	60-100	60-100
Space Velocity (hr^{-1})	7000	6000	10,000
NH_3/NO_x Mole Ratio	1.0	1.0	1.0
NO_x Removal (percent)	Over 90	Over 90	Over 90
Leak Ammonia (ppm)	Below 10	Below 10	10-20
Pressure Drop (mmH_2O)			
Reactor	100	100	50-60
Total System	250	250	100
Plant Completed	May 1974	March 1975	March 1975

The catalyst is granular and has a compressive strength of 12 kg/granule. It is placed in a fixed bed.

The results of tests made at the HNM plant are shown in Figure 4-2. They agree well with those of basic studies.

All of the plants for clean flue gas treatment have been operated trouble-free. Two plants have been operated for 3 years; Nippon Ammonia's plant has been operated for only about 10,000 hours due to the lack of ammonia production requirements. The original catalyst is still reactive and there is no plan to replace it.

4.1.3 Dirty Gas Treatment

A pilot plant and two commercial plants of Sumitomo Chemical at Sodegaura treat the dirty gas from boilers burning medium-sulfur oil. Operation data for these plants are shown in Table 4-2. A flowsheet of the two commercial plants is shown in Figure 4-3.

Both of the commercial plants are for existing boilers with a flue gas temperature of 150°C. Therefore, a heat exchanger (gas-gas heater) and an oil-fired heater were installed to heat the gas to 320°C. The No. 1 boiler has no electrostatic precipitator. A highly efficient wet electrostatic precipitator was installed to eliminate not only particulates but also SO_3 mists which affect the α-Al_2O_3 based catalyst. The reactor is of the fixed bed type. The No. 2 boiler has an electrostatic precipitator. A moving bed reactor, designed and manufactured in cooperation with Mitsubishi Heavy Industries, has been installed for the No. 2 unit.

In both units, gas heated to 320°C by the heat exchanger and heater is injected with ammonia, routed to the reactor to remove over 90 percent of the NO_x, and passed through the heat exchanger before being sent to a common stack.

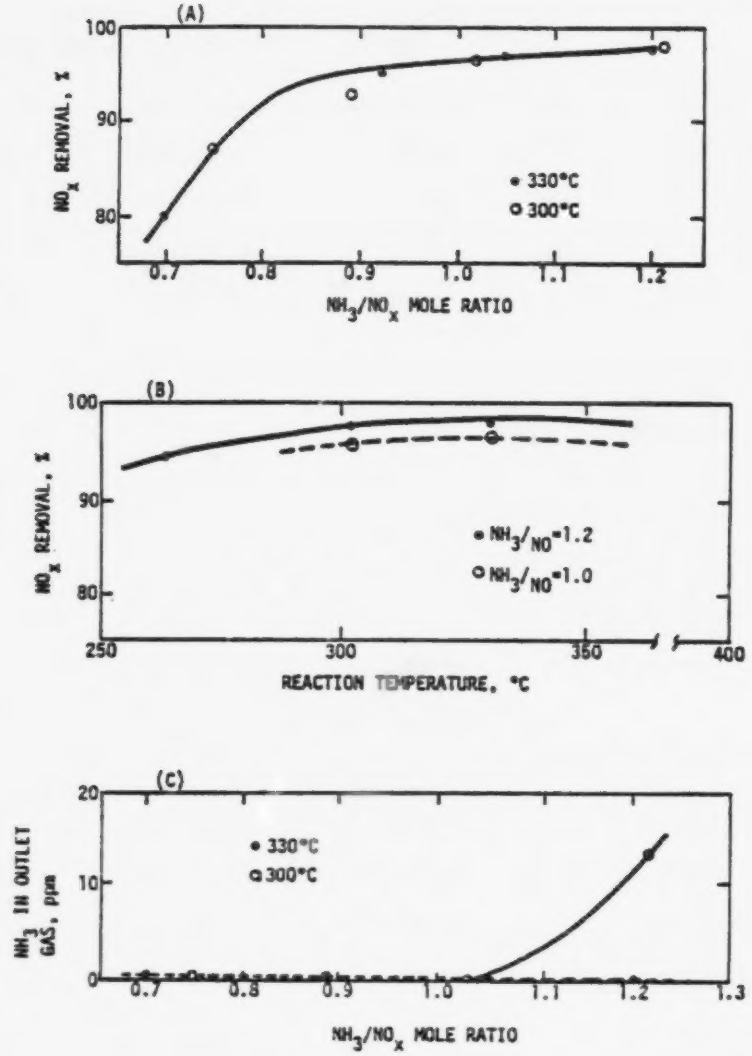


Figure 4-2. Operation data of the HNM plant and two other SCR plants.

TABLE 4-2. OPERATION DATA OF SCR PLANTS FOR DIRTY GAS

	Pilot	Commercial	
		No. 1	No. 2
Gas for SCR (Nm^3/hr)	30,000	240,000	300,000
Fuel	Oil (S=0.7%)	Oil (S=0.7%)	Oil (S=0.7%)
Load Fluctuation (percent)	60-100	60-100	60-100
Stack Height (m)	70	140	140
Inlet Gas Composition			
O_2 (percent)	6	6	6
SO_x (ppm)	400	400	400
NO_x (ppm)	200	200	200
Particulates After ESP (mg/Nm^3)	5-20	5-10	10-20
FGD Unit	None	Scheduled	Scheduled
Space Velocity (hr^{-1})	5000	5000	5000
Temperature (°C)	320	320	320
NO_x Removal (percent)	Over 90	Over 90	Over 90
NH_3/NO Mole Ratio	1.0	1.0	1.0
Leak Ammonia (ppm)	10-20	10-20	10-20
Type of Reactor	Fixed Bed	Fixed Bed	Moving Bed
Pressure Drop (mmH_2O)			
Reactor	-	200	200
Total System	-	500	500
Plant Completed	July 1973	March 1976	October 1976

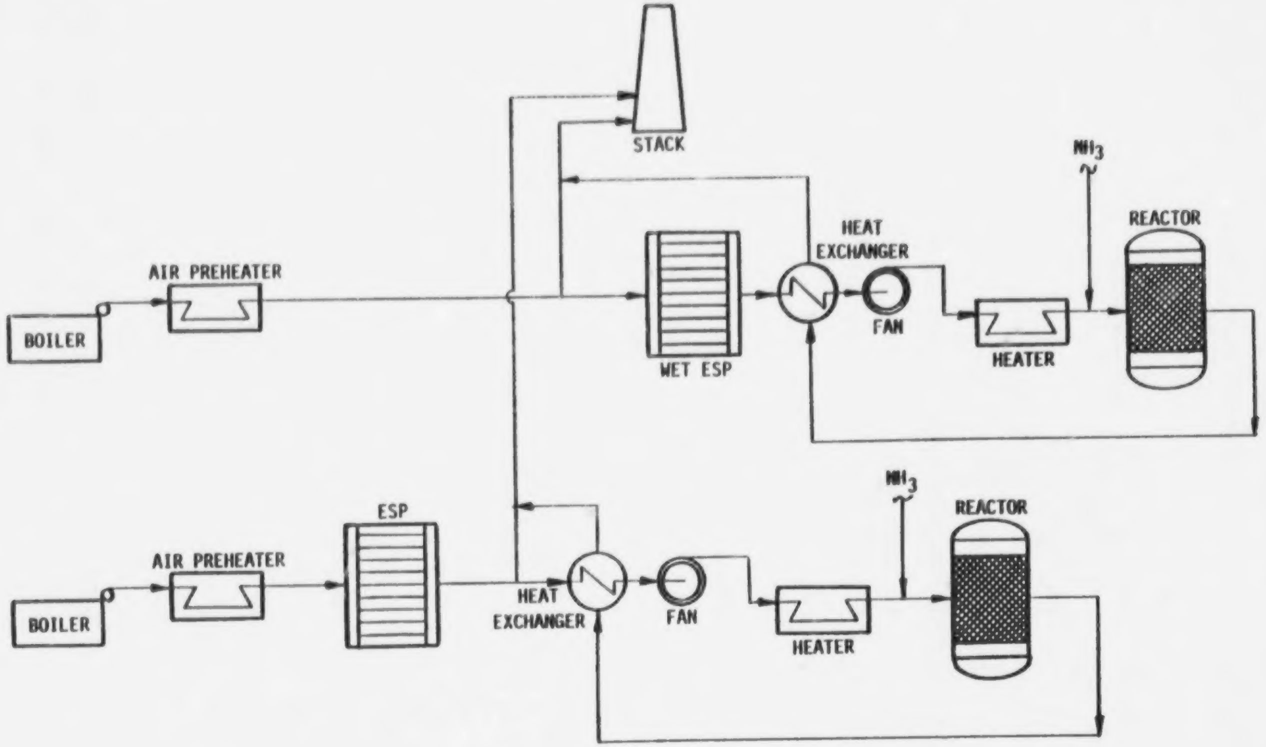

STACK
AIR PREHEATER
BOILER
WET ESP
HEAT EXCHANGER
FAN
HEATER
NH_3
REACTOR
AIR PREHEATER
BOILER
ESP
HEAT EXCHANGER
FAN
HEATER
NH_3
REACTOR

Figure 4-3. Flowsheet of two Sumitomo Chemical commercial plants for dirty gas.

The commercial plants are on boilers at ammonia plants. Since ammonia has been in oversupply and ammonia production has been stopped or slowed, the boilers and SCR plants have been operated very little since their completion.

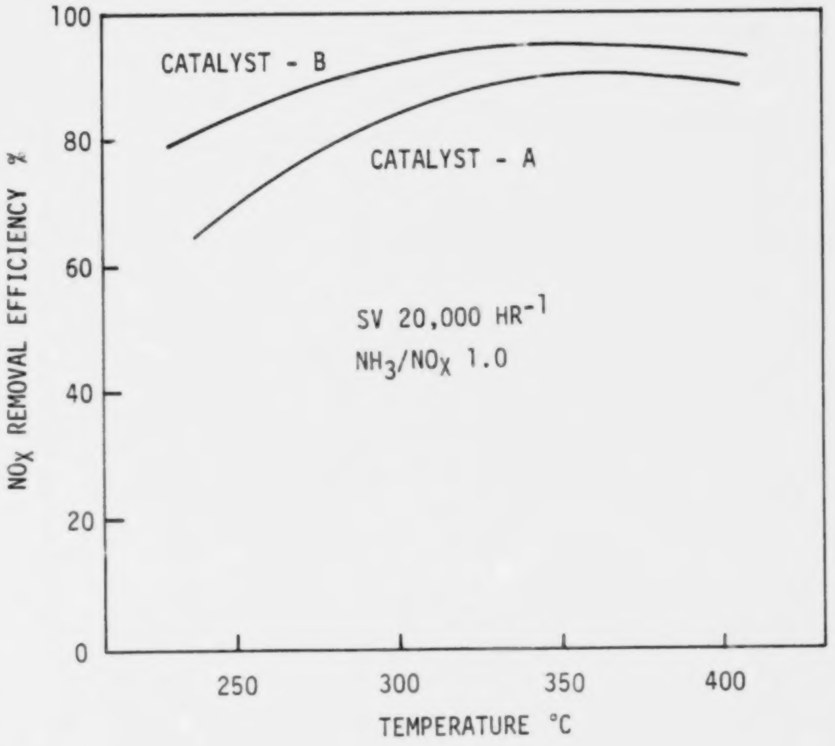
4.1.4 New Catalysts

Sumitomo Chemical has continued extensive tests on the SCR catalyst. After screening tests with several thousand samples, new catalysts have been produced. Catalyst A is based on γ-Al_2O_3 and is an improved type of the catalyst used for heating clean gas at three commercial plants since 1974. Figure 4-4 indicates that nearly 90 percent NO_x removal is obtained around 350°C at a space velocity of 20,000 hr^{-1}.

Catalyst B is based on TiO_2, more effective than A (see Figure 4-4), and resistant to SO_x. Virtually no decrease in activity was observed in two years' test with dirty gas (Figure 4-5). Catalyst C was developed earlier for use with dirty gas. It is based on α-Al_2O_3 but which showed a considerable decrease in activity after a year of use. A catalyst similar to C has been used at the two commercial plants for dirty gas (Table 4-2). Sumitomo Chemical is going to use Catalyst B commercially because it is not only SO_x-resistant, but also far more effective than Catalyst C. Ninety percent removal efficiency is obtained at a space velocity of 15,000 hr^{-1} while Catalyst C requires a space velocity of 5000 hr^{-1}. Catalyst B may also be used for clean gas. Although Catalyst B costs more than Catalyst A, Catalyst B is more efficient.

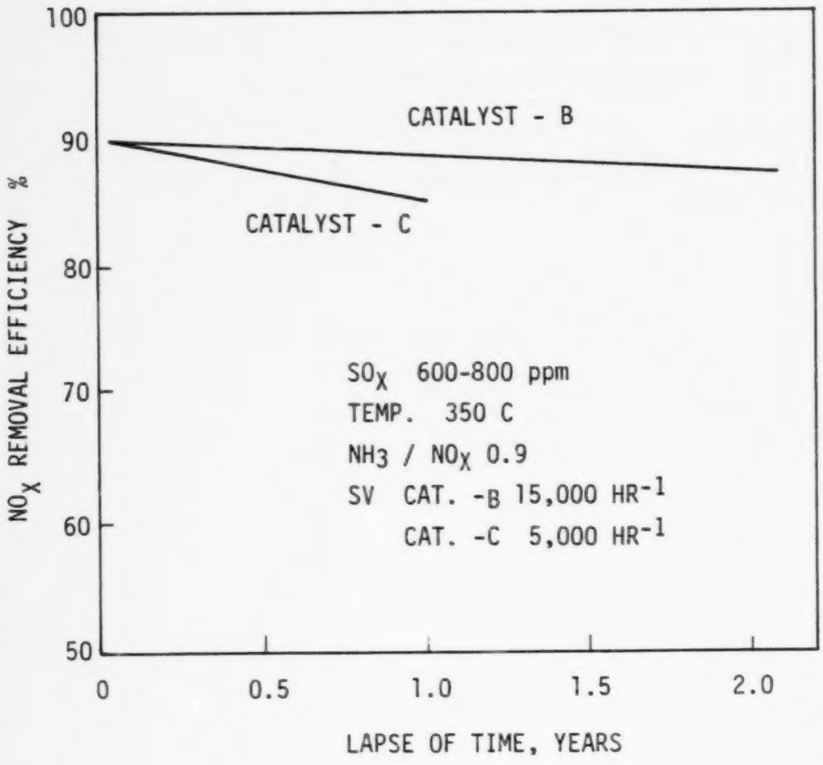
4.1.5 Economics

The HNM plant cost 250 million yen ($1,250,000) in 1973. About 800 kW are required for a blower to compensate for the pressure drop of the gas through the reactor.



CATALYST - A : Based on γ-Al_2O_3
CATALYST - B : Based on TiO_2

Figure 4-4. NO_x removal efficiency vs. reaction temperature for Catalysts A and B.



CATALYST - B : Based on TiO_2

CATALYST - C : Based on α-Al_2O_3

Figure 4-5. SO_x resistivity of Catalysts B and C.

The plant of Nihon Ammonia (250,000 Nm^3/hr of clean gas) cost 600 million yen ($3,000,000) in 1975. The cost is equivalent to 7200 yen/kW ($36/kW). The costs estimated in 1975 for plants with different capacities for clean gas treatment are shown in Table 4-3.

TABLE 4-3. ESTIMATED COST FOR CLEAN GAS TREATMENT IN 1977 FOR EXISTING BOILERS, INLET GAS 350°C, NO_x 230 PPM

	Capacity (Nm^3/hr)		
	100,000	200,000	400,000
Initial Cost (1000 yen, $5)			
Plant Cost in Battery Limit	280,000	430,000	650,000
Initial Charge of Catalyst[a]	15,000	30,000	60,000
Annual Cost (1000 yen/yr, $5/yr)			
Depreciation[b]	25,200	38,700	58,500
Interest	15,400	23,700	35,800
Catalyst	5,000	10,000	20,000
Ammonia	8,400	16,800	33,600
Power	42,000	64,000	97,000
Other	1,400	2,200	3,300
Total Annual Cost	97,400	154,000	248,200
Annualized Cost[c]			
Yen/10^3 Nm^3 ($0.005/$10^3$ Nm^3)	1,220	970	780
Yen/kl oil ($0.005/kl)	1,700	1,360	1,090
Yen/kWhr ($0.005/kWhr)	0.39	0.32	0.25

[a] SV = 20,000 hr^{-1}

[b] For 10 years

[c] 8000-hour annual operation

The plant cost for treatment of dirty gas may be more than double the cost for clean gas. A highly efficient electrostatic precipitator, heat exchanger, and heater may be required.

4.1.6 Evaluation

Sumitomo Chemical pioneered the development of SCR chemistry and technology. Its success in operating the commercial plants, including the world's first, and in producing SO_x-resistant and ammonia decomposition catalysts has encouraged other companies to develop SCR catalysts and processes. The good agreement of the results of fundamental studies with plant operation shows the reliability of the chemistry and technology developed by Sumitomo Chemical.

The plant cost, however, is relatively high presumably because the plants were constructed with extra safety to ensure long-term trouble-free operation. The newly developed TiO_2-based catalyst has outstanding features. Use of the new catalyst will not only increase the NO_x removal efficiency but also reduce the costs.

4.2 HITACHI ZOSEN (SHIPBUILDING) PROCESS

4.2.1 Introduction

Hitachi Zosen (Hitachi Shipbuilding and Engineering Co.), one of Japan's largest shipbuilding and engineering companies, has been very actively developing SCR technology for dirty gases. After tests of more than 10 pilot plants for various gases with different types of reactors and catalysts, Hitachi Zosen constructed 5 commercial plants including 3 large ones (Table 3-1). At the 3 large plants constructed in 1975 and 1976, the gases at 55-160°C are heated to about 400°C by a heat exchanger and an oil-fired heater before being sent to SCR. The heating is costly, requiring large investment and fuel oil costs.

Hitachi Shipbuilding recently began to develop honeycomb type catalysts, both ceramic and metallic, by which dirty flue gas discharged from a boiler economizer at 350-400°C can be treated directly. They have made pilot plant tests with the metallic honeycomb catalyst for flue gas from oil- and coal-fired boilers and other sources. A pilot plant funded by the United States EPA will be constructed in the United States by Hitachi Zosen with the metallic honeycomb catalyst for coal-fired boiler flue gas.

4.2.2 Catalysts

Table 4-4 lists major catalysts developed by Hitachi Zosen.

TABLE 4-4. MAJOR SCR CATALYSTS DEVELOPED BY HITACHI ZOSEN

NO_x Removal Catalysts (Noxnon)

200 Series	- 203, 204, 205, 206, 207, 208 - Cylindrical or tablet, for clean gas
300 Series	- 303, 304, 305, 306, 307, 308 - Cylindrical, spherical, and tablet, for dirty gas
400 Series	- 403, 404 - Ceramic honeycomb, for dirty gas
500 Series	- Standard type, low-temperature type and abrasion-resistant type - Metallic honeycomb, for dirty gas

NH_3 Decomposition Catalysts (Ammonon)

300 Series	- 301, 303 - Spherical, for clean and dirty gases
500 Series	- 501, 503 - Metallic honeycomb, for dirty gas

γ-Al_2O_3 is used as a catalyst carrier for clean gas, while SiO_2, SiO_2-Al_2O_3, TiO_2, or a special alloy is used for dirty gas. For catalyst metals, V, Mn, Fe, Co, Ni, Cu, Cr, W, Mo, etc. are used.

Forced tests of the deterioration of the catalysts by SO_3 have been carried out. Figure 4-6 shows the apparatus for the tests. Sulfuric acid is heated to generate SO_3 gas. The SO_3 gas is diluted to 3 percent concentration (30,000 ppm) with nitrogen gas and passed through a bed of catalyst (3 mm granules) at 400-420°C with a space velocity of 4000 hr^{-1} for periods of from 10 to 60 minutes. The catalysts which have been exposed to the SO_3 gas are then used for SCR tests at 400-420°C with a space velocity of 10,000 hr^{-1}.

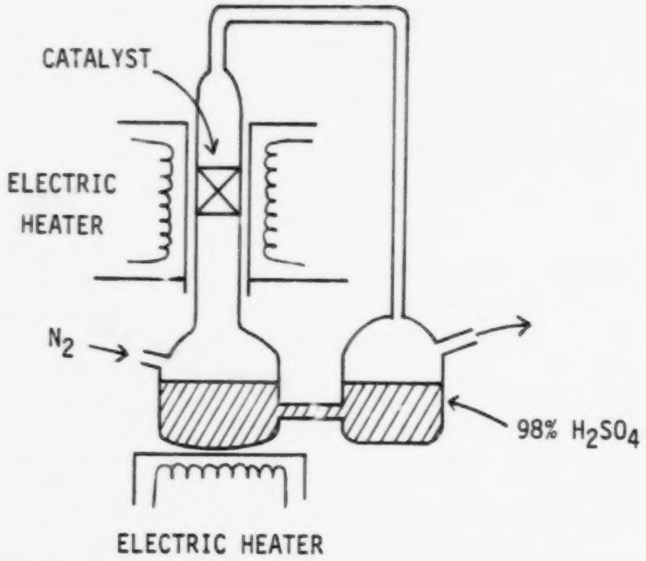


Figure 4-6. Apparatus for a test of the forced deterioration of a catalyst by SO_3.

As shown in Figure 4-7, Noxnon 203, a catalyst based on γ-Al_2O_3, was seriously affected by the SO_3-containing gas, while Noxnon 303 and 403 showed only a slight decrease in activity after the first ten minutes and virtually no further change. The NO_x removal efficiency of Noxnon 403 (about 60 percent) may be low because the space velocity is too large for the honeycomb type catalyst.

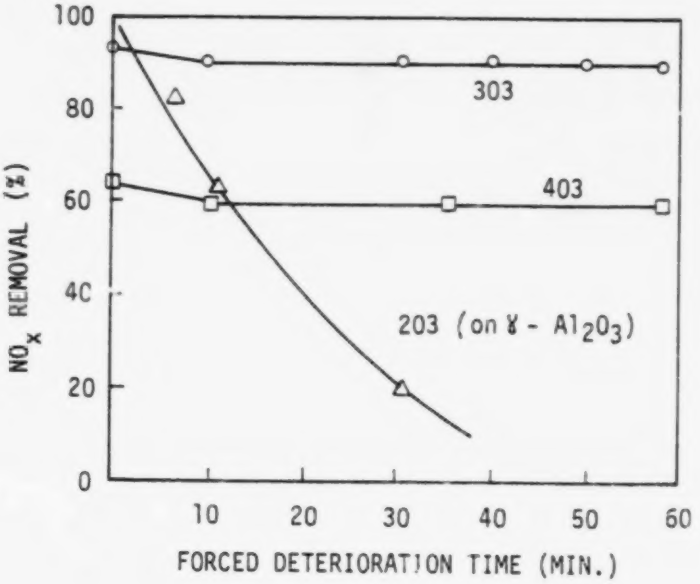


Figure 4-7. NO_x removal efficiency of Noxnon 203, Noxnon 303 and Noxnon 403 after forced deterioration of the catalyst by SO_3.

The structure of the metallic honeycomb (Noxnon 500) is shown in Figure 4-8. The catalyst is produced by etching and activating the surface of special alloy plates with a thickness of 0.5-1.0 mm. About 0.1-0.2 mm of the surface of the plates is activated. A large honeycomb with a small pitch (opening) can be made. One standard size is 0.5 x 0.5 x 0.5 m; larger honeycombs can be made.

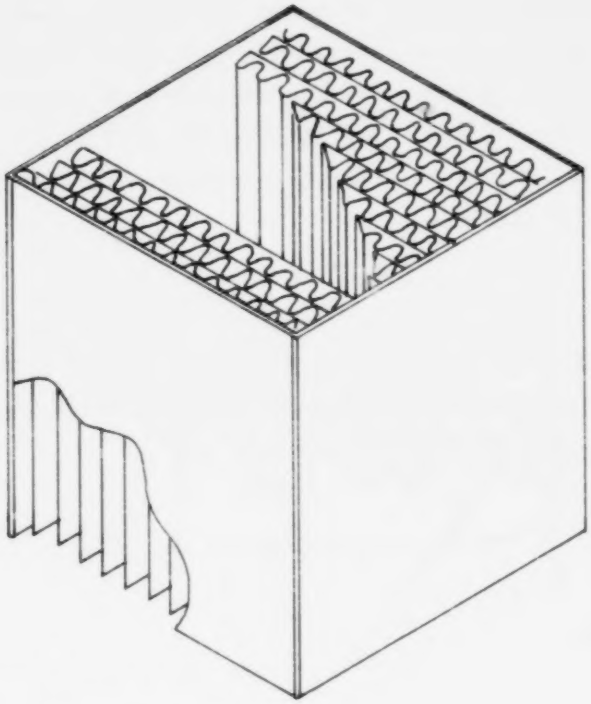


Figure 4-8. Structure of Noxnon 500.

To specify the relation between gas volume and amount of catalyst, area velocity (AV) is used instead of the space velocity, SV, for granular catalysts.

$$AV = \frac{\text{Gas rate (Nm}^3\text{/hr)}}{\text{Apparent surface area of catalyst (m}^2\text{)}}$$

The apparent surface area of the catalyst is measured assuming that the surface is flat. An AV of 8 $m^3/m^2 \cdot hr^{-1}$ is equivalent to an SV of about 5000 hr^{-1}.

The metallic honeycomb causes a small pressure drop, as shown in Figure 4-9. Since a bed depth of 1.5 m is sufficient to maintain 90 percent NO_x removal with a honeycomb with 4 mm pitch at a gas velocity of about 5 m/sec at 400°C, the pressure drop of the gas by the honeycomb for actual use is only about 40 mm H_2O.

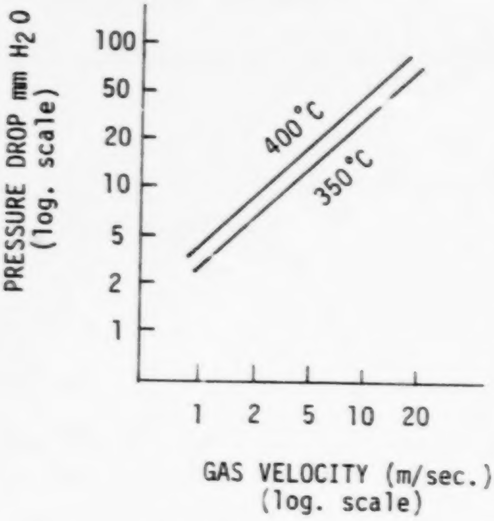


Figure 4-9. Pressure drop over 1 m of packed bed (Noxnon 500).

The NO_x removal efficiency of the Noxnon 500 catalyst as a function of temperature, NH_3/NO_x mole ratio and time obtained in a pilot plant with a flue gas from an oil-fired boiler (200 Nm^3/hr) containing 150 ppm of NO_x, 400 ppm of SO_x and 50-100 mg/Nm^3 of particulate is shown in Figures 4-10 - 4-12. Reaction temperature of about 400°C or above provides greater than 95 percent NO_x removal. Figure 4-11 indicates that over 90 percent of the NO_x was removed even at the NH_3/NO_x mole ratio of 0.8. These results indicate that the action of the metallic honeycomb may be better expressed

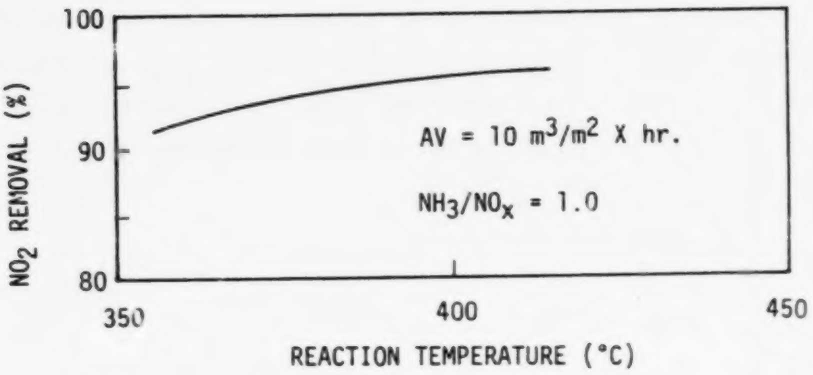


Figure 4-10. Initial efficiency of Noxnon 500 at various temperatures.

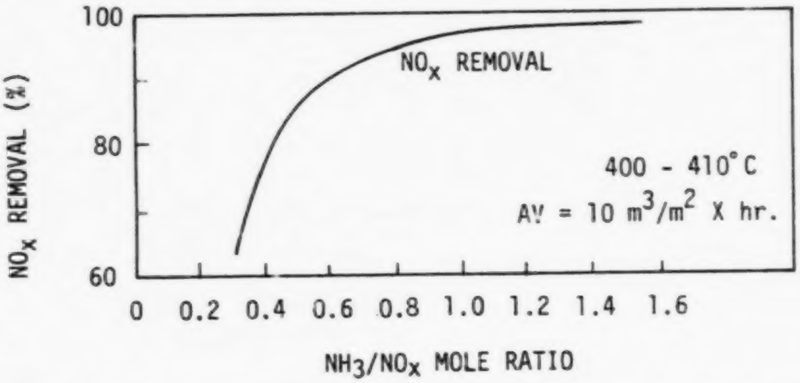


Figure 4-11. Initial efficiency of Noxnon 500 at various NH_3/NO_x mole ratios.

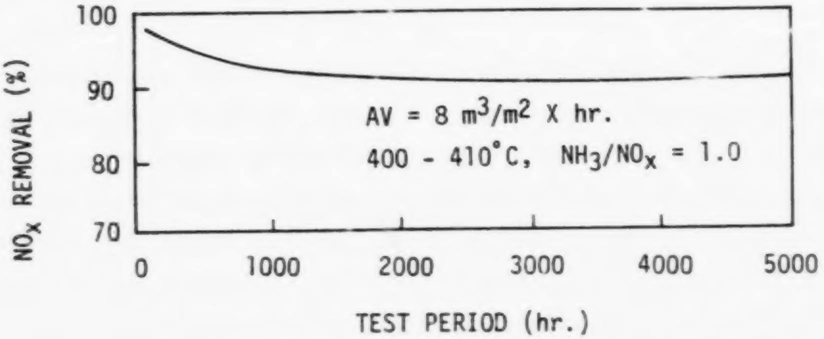


Figure 4-12. Efficiency of Noxnon 500 as a function of time.

by Equation 4-1 rather than by 4-2, which has been assumed for ceramic-based catalysts.

$$10NO + 8NH_3 + O_2 = 9N_2 + 12H_2O \qquad (4\text{-}1)$$

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad (4\text{-}2)$$

Figure 4-12 shows that the removal efficiency at an AV of 8 $m^3/m^2 \cdot hr$ was about 98 percent at first and dropped to about 90 percent after 2000 hours. No further decrease was observed.

When the metallic honeycomb becomes less reactive from contamination or from possible erosion by particulates, it can be reactivated by washing or by etching to remove the contaminated surface.

Hitachi Shipbuilding also has produced ammonia decomposition catalysts, spherical catalyst for clean gas and metallic honeycomb for dirty gas. Supposedly, 90 percent of NH_3 in the reactor outlet gas can be decomposed by the catalyst, but no details have been published.

4.2.3 Commercial Plants

Hitachi Shipbuilding constructed three large commercial SCR plants for dirty and semi-dirty gas treatment. These plants use a granular catalyst in a fixed bed (Table 4-5). The Chiba plant, Idemitsu Kosan, can treat 350,000 Nm^3/hr flue gas from a CO boiler and a furnace. This gas contains 230 ppm NO_x, 50-80 ppm SO_2, and 20-50 mg/Nm^3 particulates. The plant began operation in October 1975.

The gas at about 160°C is heated in a heat exchanger to nearly 320°C and then to 400°C by a heater. It is then treated by SCR to remove more than 90 percent of the NO_x. The gas discharged from the reactor is cooled to 260-270°C in the heat exchanger.

TABLE 4-5. OPERATION PARAMETERS OF MAJOR PLANTS CONSTRUCTED BY HITACHI ZOSEN

	Idemitsu Kosan	Shindaikyowa Petrochemical	Kawasaki Steel
Completed	Oct 1975	Nov 1975	Nov 1976
Plant Site	Chiba	Yokkaichi	Chiba
Gas Source	FCC-CO Boiler and Furnace	Oil-Fired Boiler	Iron-Ore Sintering Machine
Capacity (Nm^3/hr)	350,000	440.000	762,000
Load Factor (percent)	50-100	50-100	70-100
Pretreatment of Gas	Heating	EP*, FGD, Heating	EP, FGD WEP**, Heating
Reactor Inlet			
NO_x (ppm)	230	150	200-300
SO_x (ppm)	50-80	80-130	5-20
Particulates (mg/Nm^3)	20-50	30-100	3-10
O_2 (percent)	2.3	3.2	11.2
Reactor Type	Fixed Bed	Fixed Bed	Fixed Bed
Reaction Temperature	400	410-420	380-390
NO_x/NH_3 Ratio	1.0	1.0	1.0
Catalyst No.	204	304	304
Space Velocity (hr^{-1})	5,000	10,000	4,000
NO_x Removal (%)	93	80***	95
Pressure Drop by SCR Reactor (mmH_2O)	170	160	50
Catalyst Life	1 year	1 year	1 year

* Electrostatic precipitator.
** Wet electrostatic precipitator.
*** Leakage in heat exchanger reduced overall removal.

The plant was operated for a short time without appreciable trouble but has been shut down partly because the NO_x concentration of the gas dropped to about 100 ppm. The drop in NO_x concentration was due to a decrease in the boiler load. Another reason for the shutdown was the high operation cost requiring a large amount of fuel for heating the gas.

The second plant, Yokkaichi plant of Shindaikyowa Petrochemical, can treat 440,000 Nm^3/hr flue gas from an oil-fired boiler (Figure 4-13). The gas, which contains about 1500 ppm SO_2, 150 ppm NO_x, and 150 mg/Nm^3 particulates, is first treated by the Wellman-Lord-MKK flue gas desulfurization process to reduce the level of SO_2 to about 100 ppm and the dust level to about 50 ppm (20 ppm of the dust is a sodium salt derived from the mist of the scrubber liquor). The treated gas at 55-60°C is heated to 330-340°C in a Ljungstrom type heat exchanger and to 410-420°C by a heater. It is then subjected to SCR to reduce NO_x from about 150 ppm to 20 ppm. The gas is cooled to 160-170°C in a heat exchanger. Because land space is limited, there is no fan between the heater and the heat exchanger. The lack of a fan allows inlet gas to leak into the outlet stream. Because of this leakage, the NO_x concentration varies from 20 to 30 ppm through the exchanger.

The plant began operation in November 1975 and has been operated for 6000-7000 hours yearly, mainly because the boiler was shut down. There has been no serious trouble with the SCR unit. A catalyst on an alumina carrier was charged initially and later replaced with an improved catalyst, Noxnon 304 on a silica carrier resistant to SO_x. Major problems with the plant have been the requirement of a large amount of energy for gas heating and the deposit of ammonium bisulfate in the heat exchanger. Several soot blowings a day and an occasional water wash are required for controlling the deposit.

The third plant was installed for Kawasaki Steel at Chiba. It can treat about 800,000 Nm^3/hr flue gas from an iron-ore sintering machine.

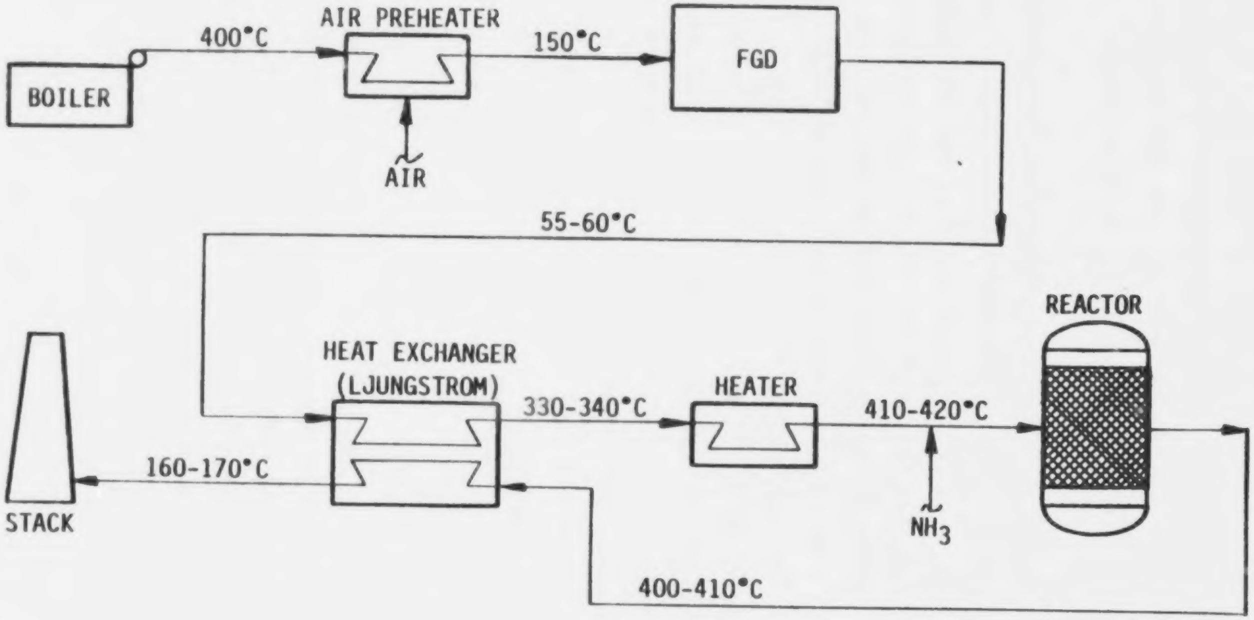

BOILER
400°C
AIR PREHEATER
AIR
150°C
FGD
55-60°C
HEAT EXCHANGER
(LJUNGSTROM)
330-340°C
HEATER
410-420°C
NH$_3$
REACTOR
400-410°C
160-170°C
STACK

Figure 4-13. Flowsheet of the Yokkaichi plant of Shindaikyowa Petrochemical.

The gas contains 200-300 ppm NO_x and 300-400 ppm SO_2 particulates. It is first treated with an electrostatic precipitator to reduce the particulate level to 70 mg/Nm^3, and then by the MHI lime-gypsum flue gas desulfurization process to reduce the SO_2 concentration to about 10 ppm. The gas is then passed through a wet electrostatic precipitator to reduce the particulate concentration to below 10 mg/Nm^3. The cleaned gas is passed through a heat exchanger, heater and subjected to SCR. The plant began operation in November 1976 and has operated smoothly since then. The high degree of gas cleaning prior to SCR is helpful but both investment and operation costs seem high. Ammonium bisulfate is not an appreciable problem because of the low SO_3 content of the gas; SO_3 is caught partly by FGD and predominantly by the wet electrostatic precipitator.

4.2.4 Economics

The costs estimated by Hitachi Zosen for treating gas from oil-fired boilers with different capacities (33-500 MW) using a low-sulfur oil (S below 0.5 percent) and high sulfur oil (S = 3 percent) are shown below. The following systems with each of the two fuels were assumed for the estimation (Figure 4-14).

I. Low-sulfur oil (no desulfurization)
   a) SCR is applied to the gas which leaves a boiler economizer at about 400°C. After the SCR, the gas is passed through an air preheater and an electrostatic precipitator and sent to a stack at 200°C.
   b) The gas leaving an air preheater and electrostatic precipitator at 150°C is heated to 400°C by a heat exchanger and an oil-fired heater and then subjected to SCR. The gas leaving the SCR reactor at 400°C is passed through a heat exchanger and then sent to a stack at 220°C.

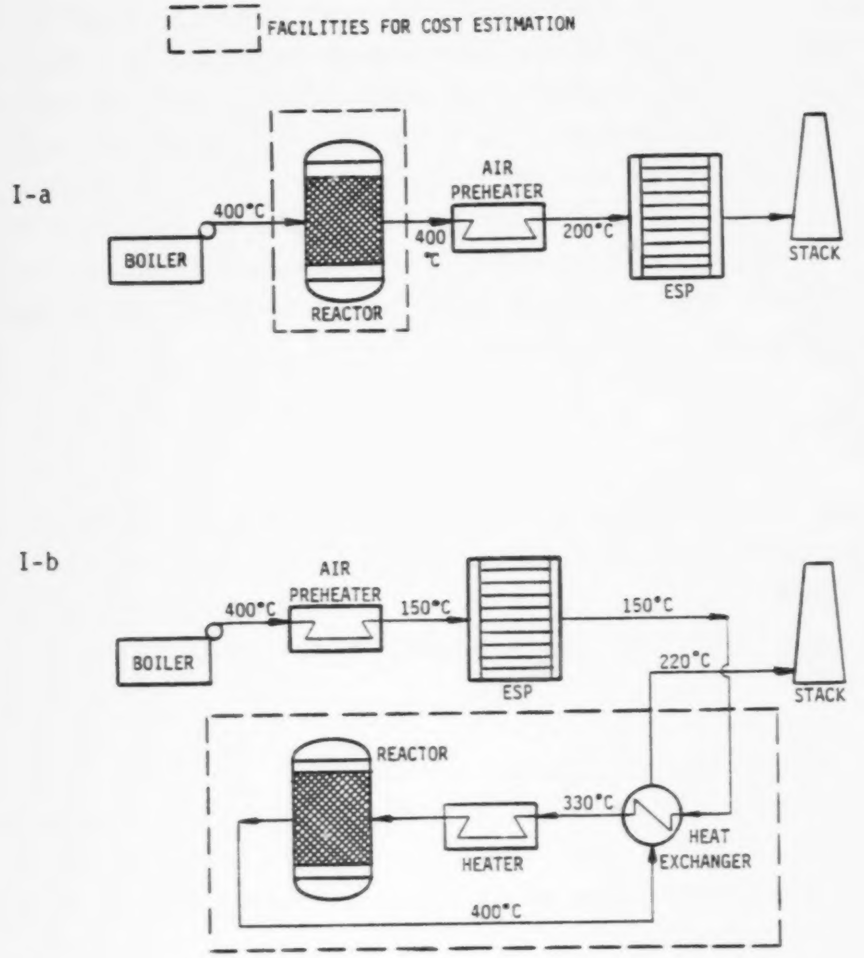

FACILITIES FOR COST ESTIMATION
I-a
400°C
BOILER
REACTOR
400 °C
AIR PREHEATER
200°C
ESP
STACK
I-b
400°C
BOILER
AIR PREHEATER
150°C
ESP
150°C
220°C
STACK
REACTOR
HEATER
330°C
HEAT EXCHANGER
400°C

Figure 4-14. Hitachi Zosen systems assumed for a cost estimate.

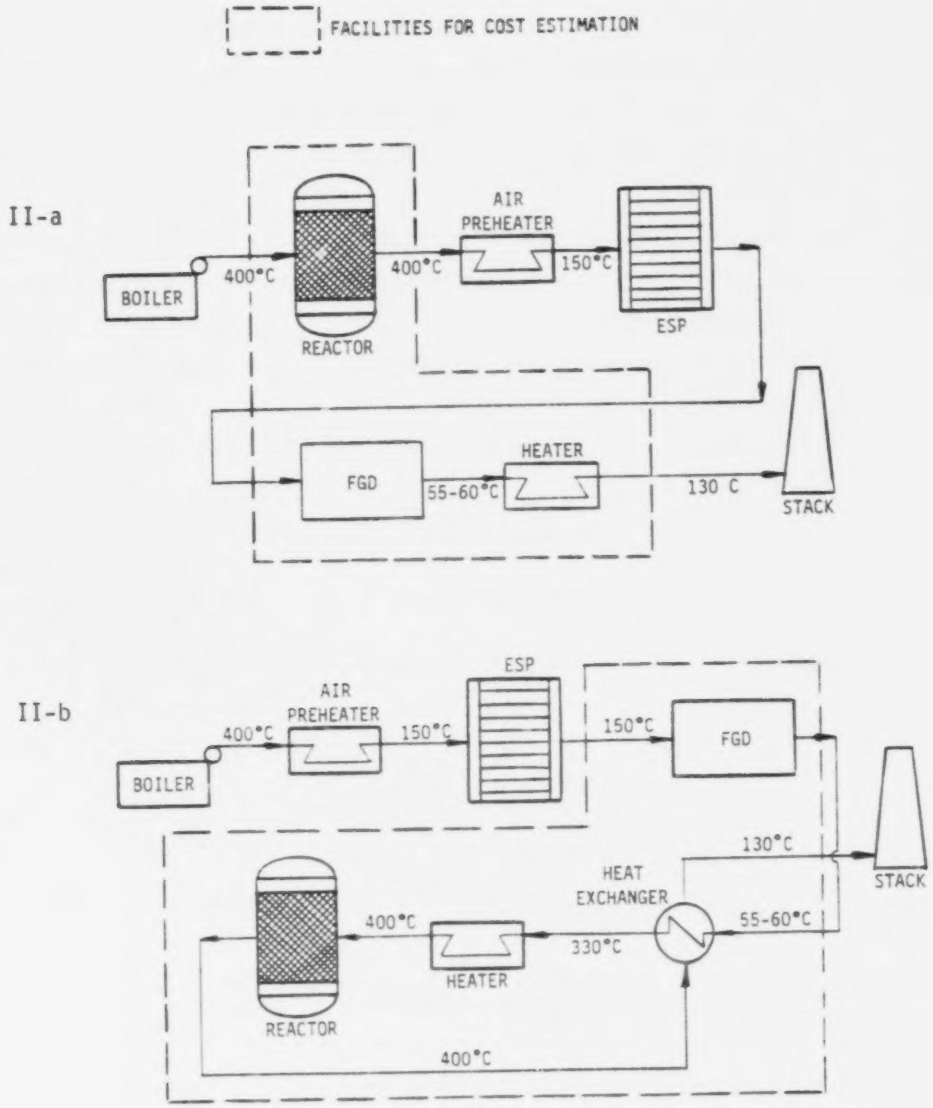

FACILITIES FOR COST ESTIMATION
II-a
BOILER
400°C
REACTOR
400°C
AIR PREHEATER
150°C
ESP
FGD
55-60°C
HEATER
130 C
STACK
II-b
BOILER
400°C
AIR PREHEATER
150°C
ESP
150°C
FGD
STACK
130°C
HEAT EXCHANGER
55-60°C
330°C
HEATER
400°C
REACTOR
400°C

Figure 4-14. (Continued).

II. High sulfur oil (FGD)

a) SCR is applied to the gas which leaves a boiler economizer at about 400°C. After the SCR, the gas is passed through an air preheater and an electrostatic precipitator. It then proceeds to an FGD system using the limestone/gypsum process. The gas is then reheated to 130°C and led to a stack.

b) The gas leaving an air preheater and electrostatic precipitator at 150°C is first subjected to FGD by the limestone/gypsum process. The gas, cooled to 55-60°C, is heated by a heat exchanger and heater to about 400°C and subjected to SCR. The gas leaving the reactor at 400°C is passed through the heat exchanger to cool to 130°C and is then sent to a stack. The system is similar to that of the Yokkaichi plant, Shindaikyowa Petrochemical (Figure 4-13), except that better heat recovery is assumed.

The assumptions for the cost estimation are shown below:

a) NO_x content of gas
  150-180 ppm for low-sulfur oil
  260-300 ppm for high-sulfur oil

b) NO_x removal efficiency--90 percent

c) SO_x removal efficiency--90 percent

d) Number of scrubbers and reactors
  One scrubber and one SCR reactor up to 1,000,000 Nm^3/hr of gas (330 MW equivalent). Two scrubbers and two reactors are needed for larger capacity.

e) Catalyst cost--1.5 million yen for 1 MW ($75,000/MW)

f) Catalyst life--1 year

g) Operation hours--8000 hours yearly

h) Depreciation--7 years

i) Interest--10 percent per year

j) Maintenance cost--3 percent of investment per year

k) Tax and insurance--2 percent of investment per year

l) Labor

For SCR only (low-sulfur oil)--1 person/shift/reactor

For SCR and FGD (high-sulfur oil)

- Below 330 MW--3 persons/shift plus 5 persons in daytime
- Above 330 MW--3 persons/shift plus 7 persons in daytime
- Yearly salaries--3 million yen per person ($15,000/person)

m) Fuel oil for reheating--25 yen/10,000 kcal ($0.125/10,000 kcal)

n) NH_3--80 yen/kg ($0.40/kg)

o) $CaCO_3$--3 yen/kg ($0.015/kg)

p) Power--12 yen/kWhr ($0.06/kWhr)

q) By-product gypsum--no value

Investment and annualized costs for the application of SCR to gas from low-sulfur oil burning are shown in Figure 4-15. The investment for system I-a, which treats gas from a boiler economizer, includes a reactor, ammonia storage and vaporizer, a fan to compensate for a pressure drop of 110

mmH_2O, and instruments for measurement and control. System 1-b, which treats gas from an air heater, includes a heat exchanger and heater in addition to the equipment of System I-a.

The investment cost for System I-a with a capacity larger than 300 MW is about 4000 yen/kW ($20/kW). Costs for System I-b are almost double because of the added cost of the heat exchanger and heater. There would be no cost advantage of scaling the system above 330 MW, because two trains would then be needed. The annualized costs at 300 MW are about 0.4 yen/kWhr ($0.002/kWhr) for I-a and about 0.8 yen/kWhr ($0.004/kWhr) for I-b.

Figure 4-16 shows the costs for SCR followed by FGD (System II-a). SCR accounts for about 20 percent of the total investment and 25 percent of the total annualized costs. The SCR costs are virtually the same as those shown for System I-a of Figure 4-15. The total investment cost for 300 MW is about 24,000 yen/kW ($120/kW) and the total annualized cost of 300 MW is about 1.65 yen/kWhr ($0.008/kWhr).

The costs for FGD followed by SCR (System II-b) are shown in Figure 4-17. For a 300 MW plant, the total investment cost is 28,000 yen/kW ($140/kW) and the total annualized cost is 1.9 yen/kWhr ($0.009/kWhr). SCR accounts for about 35 percent of the investment and nearly 50 percent of the annualized costs. The Yokkaichi SCR plant, Shindaikyowa (150 MW equivalent) is said to have cost about 2 billion yen ($10 million) in 1976 including the heat exchanger, while Figure 4-17 shows that a similar plant costs 1.5 billion yen ($7.5 million). Recent improvements in technology have resulted in the considerable cost reduction.

The annualized cost of FGD as shown in Figure 4-16 is about 20 percent higher than that shown in Figure 4-17 because the former includes the cost for reheating the gas after FGD to 130°C. When the reheating temperature is 80°C, the cost difference is 6 percent.

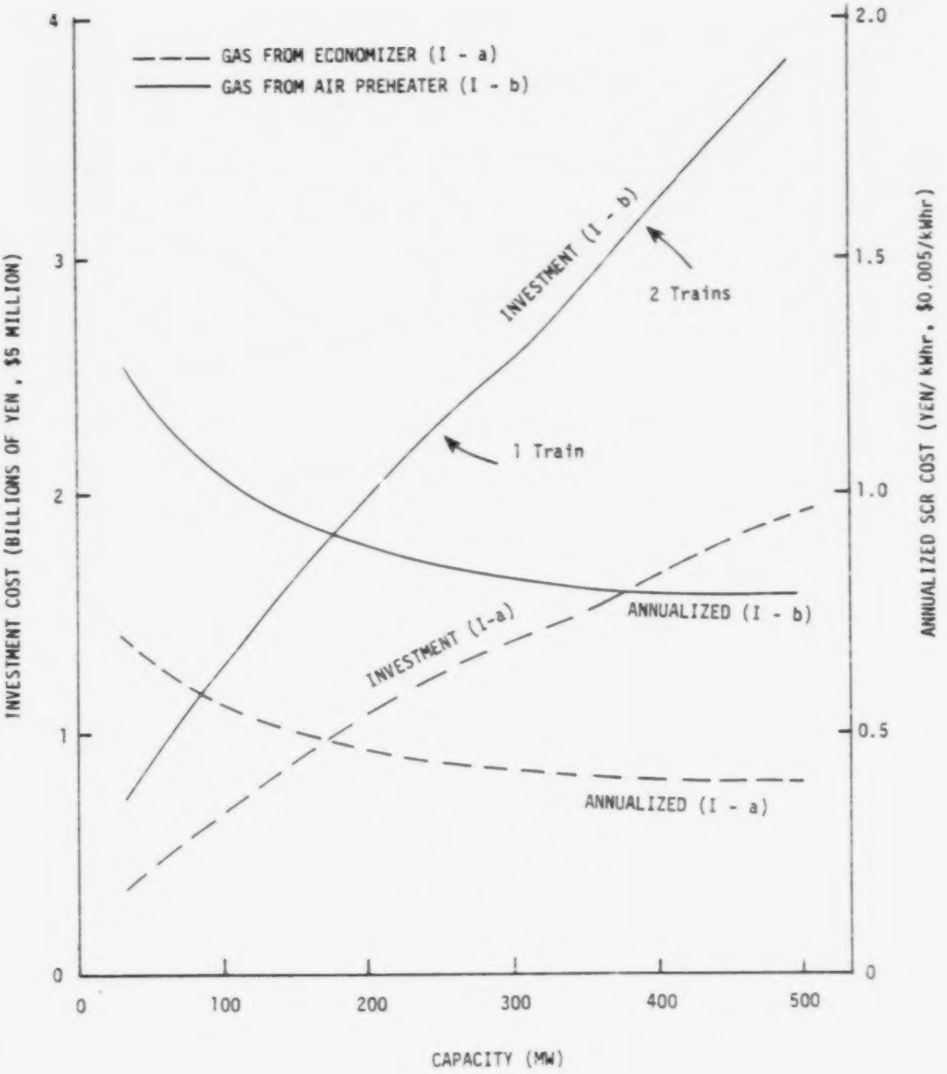


Figure 4-15. Estimated cost for SCR by Systems I-a and I-b.

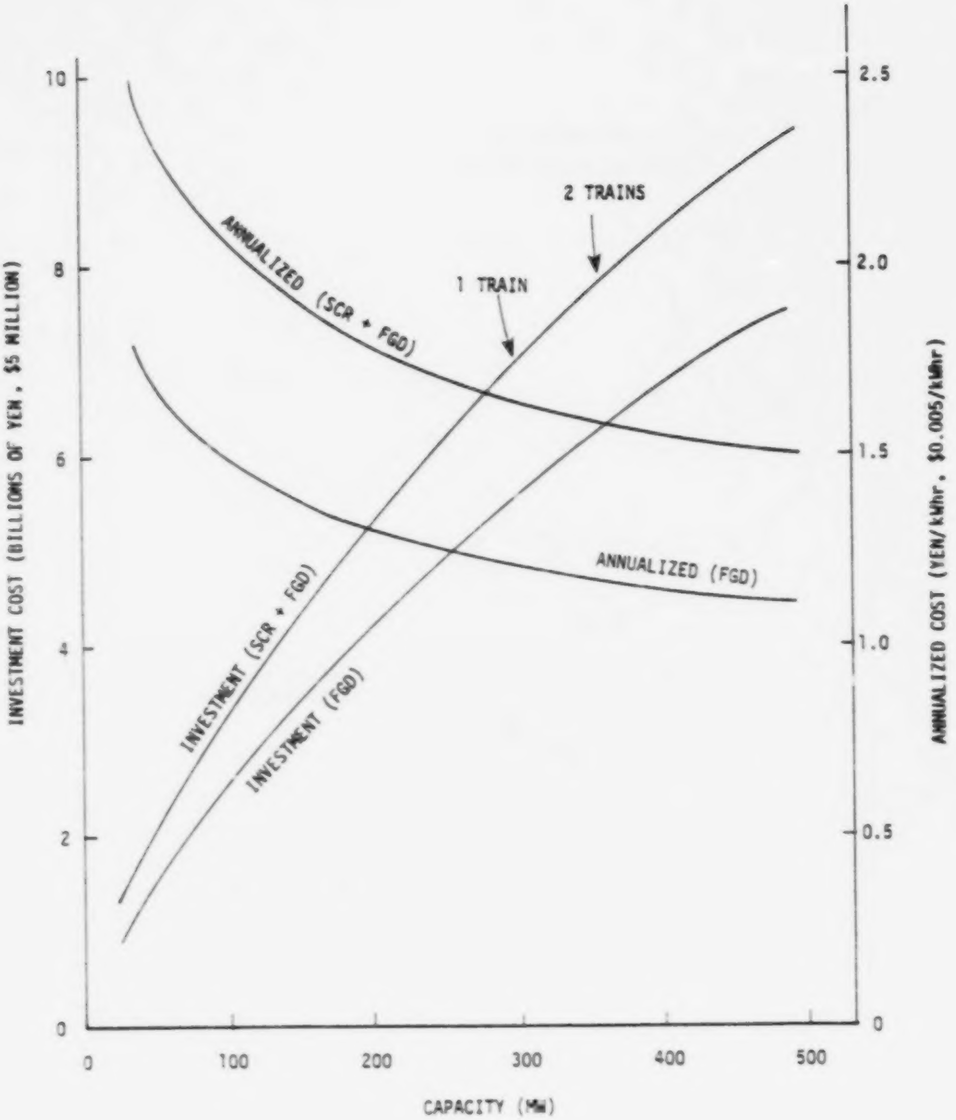


Figure 4-16. Estimated cost of SCR followed by FGD (System II-a).

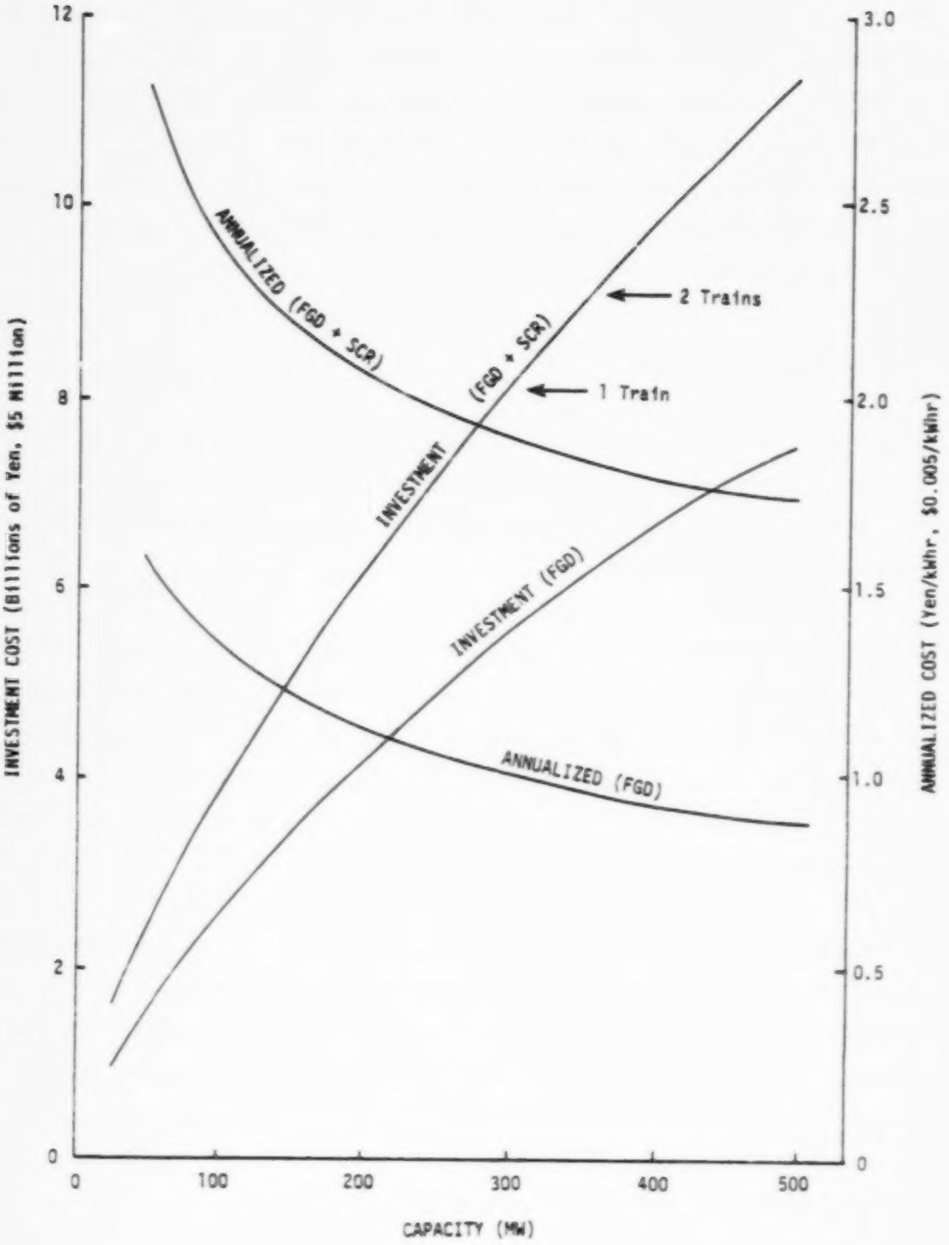


Figure 4-17. Estimated cost of FGD followed by SCR (System II-b).

Hitachi Shipbuilding has also made a cost estimate for the treatment of flue gas from a coal-fired boiler. Roughly speaking, the investment cost is about 15 percent higher and the annualized cost nearly 20 percent higher than those for the treatment of gas from an oil-fired boiler with an equal SO_x concentration. The higher cost is due largely to the larger gas volume (about 20 percent more for coal than for oil for an equal MW) and the much higher NO_x concentration (500-600 ppm for coal).

4.2.5 Evaluation

When Hitachi Shipbuilding constructed large commercial plants in 1975 and 1976, neither SO_x-resistant catalysts nor parallel flow type reactors had been well developed; pretreating the gas with FGD was the only feasible method for controlling SO_x.

Comparison of Figures 4-16 and 4-17 indicates that the total annualized cost for SO_x and NO_x removal by System II-b is about 16 percent higher than that for removal by System II-a. Lowering the gas reheating temperature in System II-a to 80°C will cut the annualized cost by about 10 percent, so that the difference in cost between System II-a and System II-b will be about 25 percent.

An ammonium bisulfate deposit in the air preheater will be a problem with System II-a. In System II-b, SO_3 not sufficiently removed by FGD will be a problem for the heat exchanger. This problem has been experienced at the Yokkaichi plant, Shindaikyowa. The soot blow and possible water wash required may add some cost. The problem may not be serious for Systems I-a and I-b because of the low sulfur content of the fuel and the high gas temperature in the air preheater and heat exchanger.

The metallic honeycomb developed by Hitachi seems promising because of the large size which eases packing, the low pressure drop which saves energy, and the high NO_x removal efficiency at low NH_3/NO_x ratio. On the other hand, the catalyst may have the following drawbacks:

1) Erosion by fly ash may lower the activity since the activated surface is very thin (about 0.15 mm). A moderate gas velocity should be used to avoid the erosion.

2) The catalyst is most efficient at 400°C or higher. A heating device may be required for existing boilers whose economizer outlet temperature fluctuates between 300 and 400°C.

Further study is desired to produce large SO_x-resistant honeycombs reactive between 300 and 400°C. Such a type of catalyst is under development by Hitachi Zosen. The U.S. EPA recently awarded a contract to Hitachi Zosen for pilot scale (approximately 0.5 MW) study of the metal honeycomb catalyst. Hitachi Zosen has subcontracted Chemico Air Pollution Corp. to build and operate the unit which is to be sited at a coal-fired boiler at Georgia Power Company's Mitchell Station. The tests will provide information for further evaluation.

4.3 HITACHI LTD. PROCESS

4.3.1 Introduction

Hitachi Ltd., one of the largest boiler and machine makers in Japan, has studied SCR processes at more than 10 pilot plants. They can treat 200-4000 Nm^3/hr of various gases, including gas from a coal-fired boiler. Hitachi Ltd. had constructed by April 1, 1978, 8 commercial plants with capacities larger than 10,000 Nm^3/hr, including very large plants for two 700 MW LNG-burning boilers (Tables 3-1 and 4-6). In addition, Hitachi Ltd. recently constructed 3 prototype plants for oil-fired utility boilers (Table 4-6).

TABLE 4-6. SCR PLANTS BUILT BY HITACHI LTD. (LARGER THAN 10,000 NM^3/HR)

Plant Owner (Site)	Gas Source (Fuel)	Capacity Nm^3/hr (MW)	Gas Pre-treatment	Reactor Type	Catalyst Shape	Reaction Temp, °C	SV Hr^{-1}	NO_x Removal	Completion
Kawatetsu Chem. (Chiba)	Coke Oven (COG)	500,000 (165)	ESP Heating	Vertical (Movable)[a]	Ring	335	6200	95	Oct 1976
Chiyoda Kenzai (Kaizuka)	Boiler (Heavy Oil)	15,000 (5)	None	Vertical (Movable)	Ring	335	6000	70	Sept 1976
Kansai Electric (Kainan)	Boiler (Heavy Oil)	300,000 (¼ of 450)	None	Horizontal (Fixed)	Ring	385		80	June 1977
Nisshin Steel (Amagasaki)	Boiler (Heavy Oil)	20,000 (7)	Heating	Vertical (Movable)	Ring	335	6000	90	July 1977
Kansai Paint (Amagasaki)	Boiler (Kerosene)	16,000 (5)	Heating	Vertical (Movable)	Ring	335	6000	90	Oct 1977
Chubu Electric (Chita)	Boiler (LNG)	1,910,000x2 (700x2)	None	Horizontal (Fixed)	Pellet	350		80	Mar 1978
Nippon Oils & Fats (Amagasaki)	Boiler (Heavy Oil)	20,000 (7)	None	Vertical (Movable)	Ring	350	6000	90	Apr 1978
Company A	Boiler (Kerosene)	30,000 (10)	Heating	Vertical (Movable)	Ring	280	6000	90	Sept 1978
Company B	Boiler (Heavy Oil)	482,600 (175)	SNR[b]	Parallel Flow	Plate	355		50[c]	July 1978
Company C	Boiler (Heavy Oil)	466,000 (156)	None	Parallel Flow	Plate	385		30	July 1978

[a] Intermittent moving.
[b] Selective noncatalytic reduction.
[c] Total of SNR and SCR.

Hitachi Ltd. has studied many types of catalysts, including the Rashig ring type and the plate type catalysts being used for large-scale tests with utility boiler flue gas.

4.3.2 Catalysts and Reactors

A flowsheet of the SCR system for boiler flue gas is shown in Figure 4-18.

Combinations of types of catalyst and reactor selected by Hitachi Ltd. for different gas compositions are shown in Table 4-7. The Raschig ring type catalyst not only has a large surface area and is highly effective; it is less vulnerable to dust plugging because of its large size. Its diameter is about 15 mm, compared to about 5 mm for most granular catalysts. The dust deposition ratio (dust deposits on catalyst bed/percent of total) depends upon the size of the catalyst as shown in Figure 4-19. The ring is strong enough for use in a moving bed. Test results with the ring catalyst are shown in Figures 4-20 - 4-22 for NO_x removal and NH_3 leakage as a function of SV and NH_3/NO_x ratio.

Hitachi Ltd. has developed a plate catalyst for particulate-rich gas. A powdered catalyst is cemented on a thin metal plate; total thickness is about 1 mm. The plates are placed in a basket in parallel and the baskets are placed in a reactor. Test results with the catalyst are shown in Figures 4-23 - 4-25 for NO_x removal as a function of SV, temperature, and NH_3/NO_x ratio.

Figure 4-26 shows an example of the structure of a large reactor with the parallel plate catalyst. The catalyst plates are placed in baskets, each measuring about 1 m x 1 m x 1 m, and the baskets are placed in the reactor in 4 layers. The gas passes through the baskets downwards so that the dust is readily blown down to keep the catalyst surface clean.

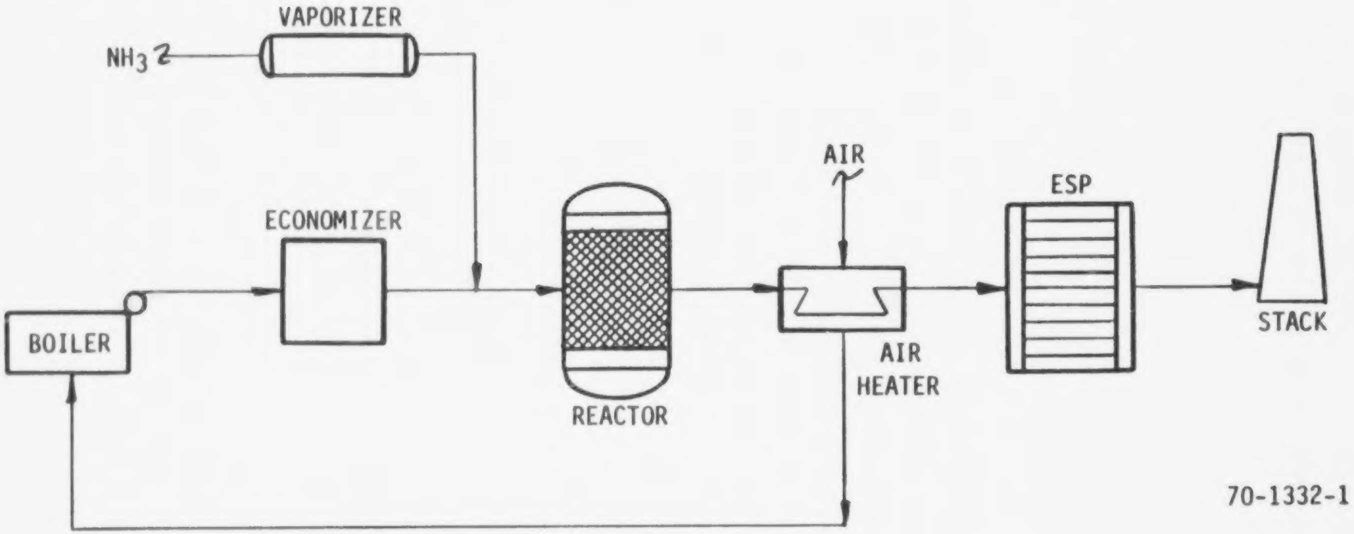

VAPORIZER
NH₃
ECONOMIZER
BOILER
REACTOR
AIR
AIR HEATER
ESP
STACK
70-1332-1

Figure 4-18. Flow diagram of the direct system for boiler flue gas at Hitachi, Ltd.

TABLE 4-7. CATALYSTS AND REACTORS SELECTED BY HITACHI, LTD. FOR SEVERAL GASES

Gas	Fuel	Reactor	Catalyst
Clean	LNG	Fixed Bed	Pellet Sphere
Semi-Dirty	Kerosene Low-S Oil	Fixed Bed	Pellet Ring Sphere Plate
		Movable Bed*	Pellet Sphere Ring
Dirty	High-S Oil	Movable Bed*	Ring
		Fixed Bed	Plate

* Intermittent moving.

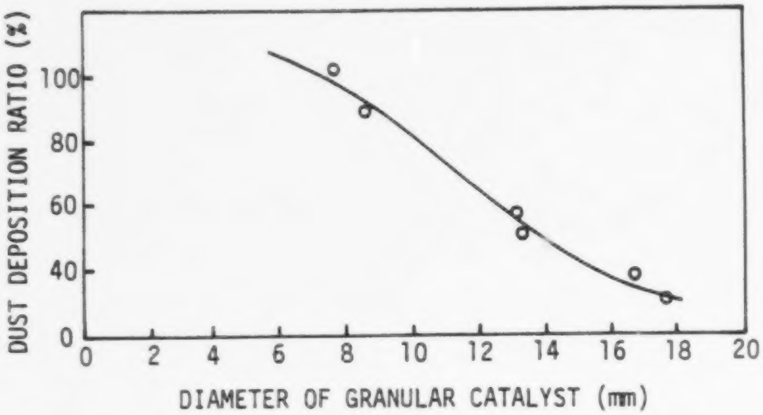


Figure 4-19. Catalyst size versus dust deposition for oil-fired dust.

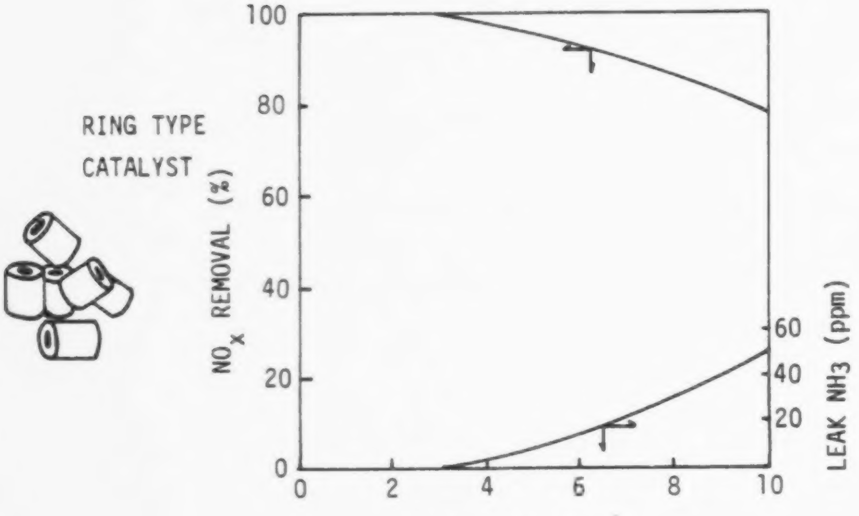


Figure 4-20. SV versus NO$_x$ removal and NH$_3$ leak (ring type catalyst, 15 mm diameter; 350°C; NH$_3$/NO, 1.0; Inlet NO$_x$, 250 ppm).

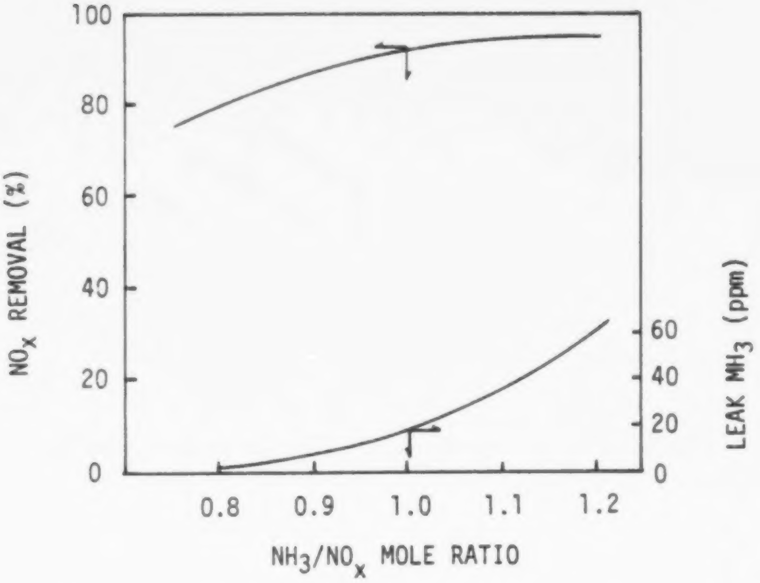


Figure 4-21. Effect of NH_3/NO_x mole ratio on the performance of a ring catalyst (15 mm diameter; SV, 6200 hr^{-1}; 350°C; inlet NO_x, 250 ppm).

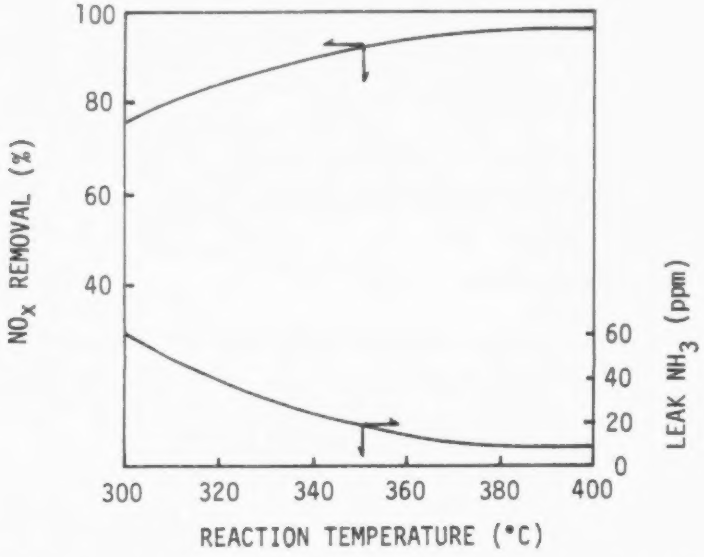


Figure 4-22. Effect of temperature on the performance of a ring catalyst (15 mm diameter; 350°C; SV, 6200 hr^{-1}; NH_3/NO, 1.0; inlet NO_x, 250 ppm).

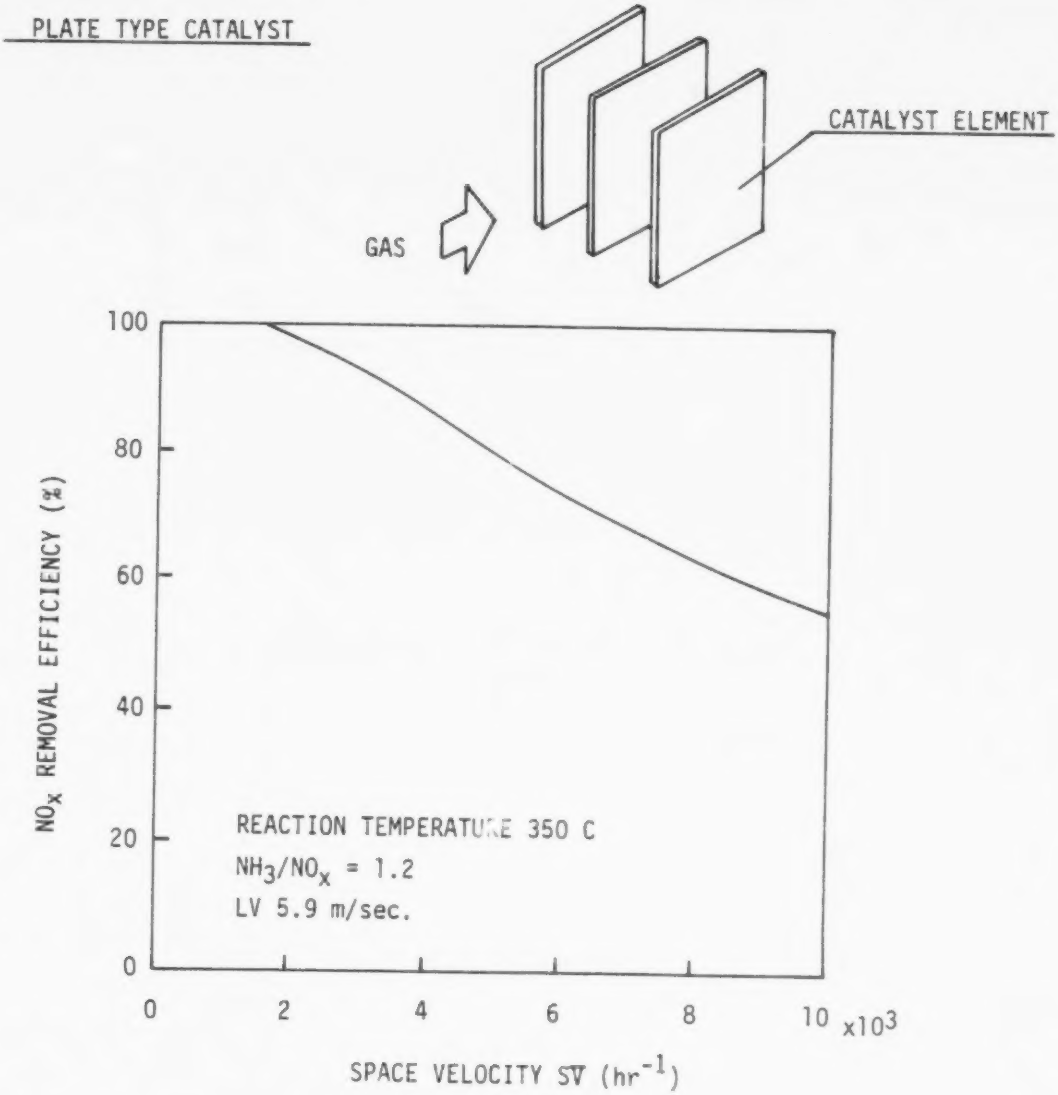


Figure 4-23. Characteristic curve of space velocity versus NO_x removal efficiency by a plate catalyst.

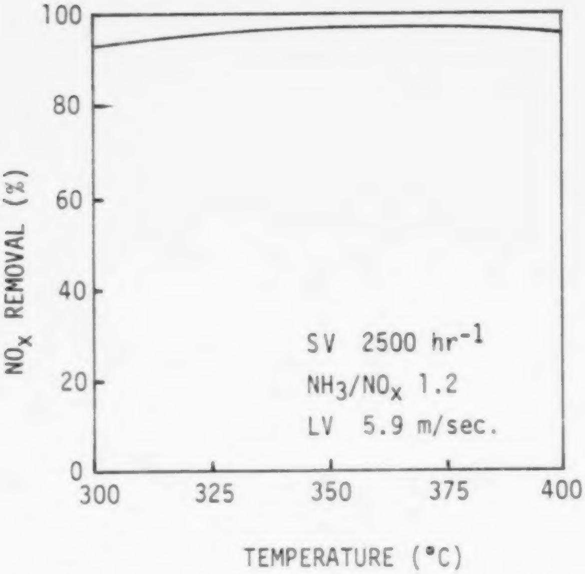


Figure 4-24. Reaction temperature versus NO_x removal for a plate catalyst.

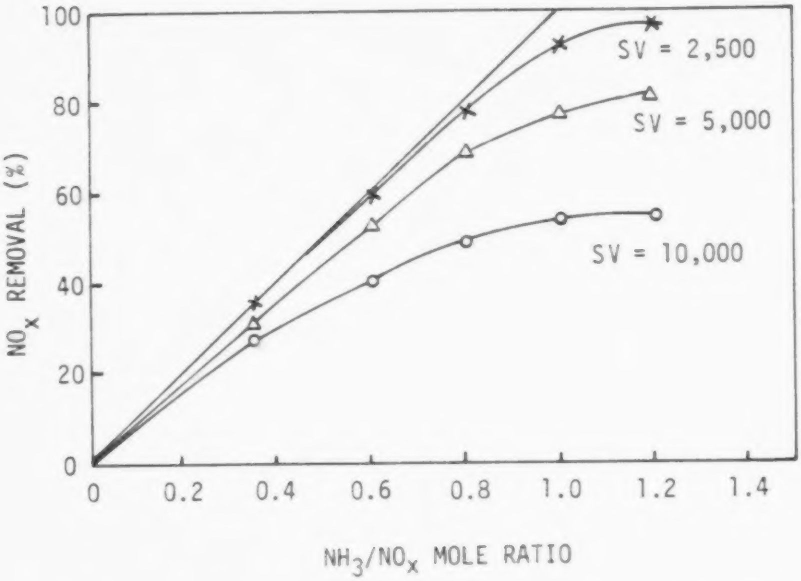


Figure 4-25. NH_3/NO_x mole ratio versus NO_x removal for a plate catalyst at 350°C, LV = 5.9 m/sec.

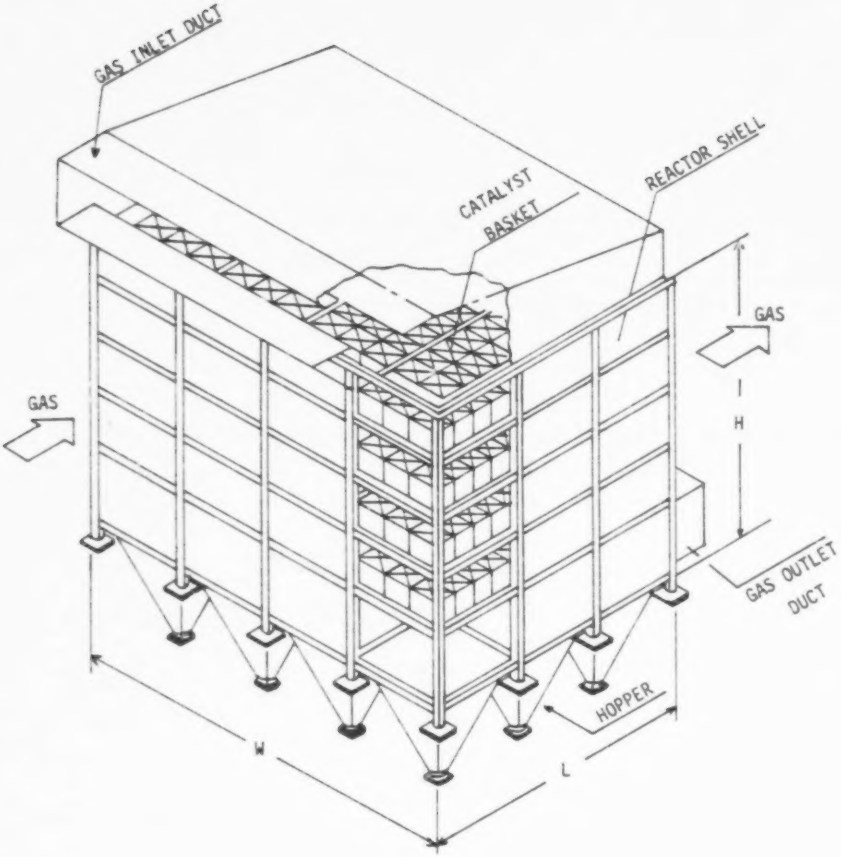

GAS INLET DUCT
CATALYST BASKET
REACTOR SHELL
GAS
GAS
H
GAS OUTLET DUCT
HOPPER
W
L

Figure 4-26. Structure of parallel plate reactor.

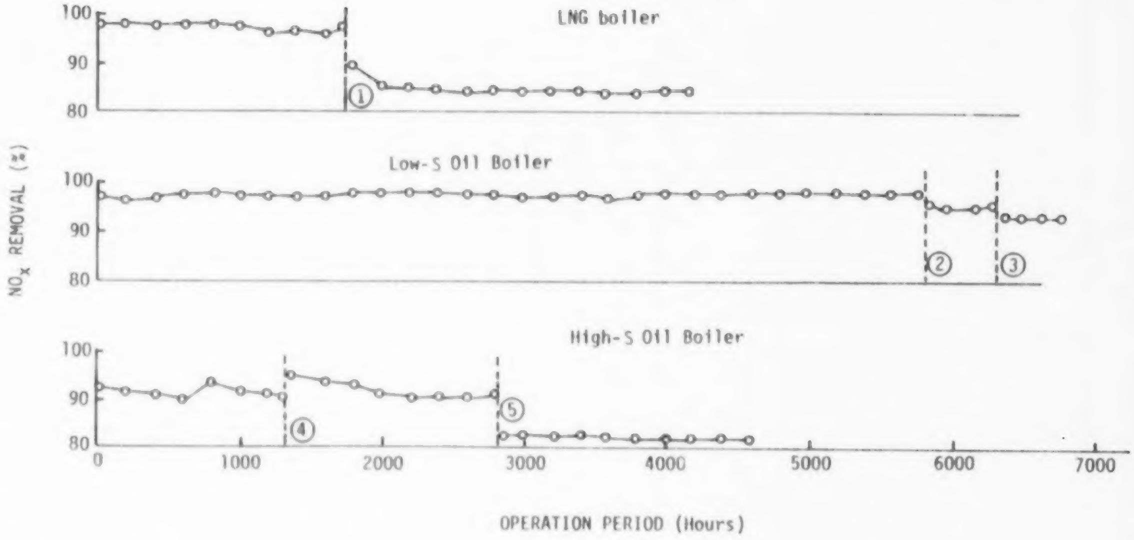
4.3.3 Pilot Plant Tests

Some of the results of pilot plant tests with gases from gas- and oil-fired boilers are shown in Figure 4-27. These plants use the ring type catalyst in a fixed bed. About 97 percent of the NO_x was removed from LNG boiler flue gas at 350°C, with an SV of 10,000 hr^{-1} and an NH_3/NO_x mole ratio of 1. Increasing the SV to 20,000 hr^{-1} lowered the NO_x removal efficiency to 85 percent.

For flue gas from low sulfur oil, the removal efficiency was about 97 percent at an SV of 10,000 hr^{-1}, 94 percent at 15,000 hr^{-1}, and 90 percent at 20,000 hr^{-1}. An SO_x-resistant catalyst was used for the test and showed virtually no degradation after 7000 hours of use.

For flue gas from high sulfur oil, 90-95 percent NO_x removal efficiency was obtained at an SV of 6200 hr^{-1} with an NH_3/NO_x mole ratio of 0.95. The efficiency increased slightly at an SV of 4500 hr^{-1} and decreased to about 83 percent at an SV of 6200 hr^{-1} with an NH_3/NO_x mole ratio of 0.83. The NH_3 leakage was kept below 5 ppm by keeping the NH_3/NO_x mole ratio below 1.0, and thus the deposit of ammonium bisulfate in the air preheater was reduced and could be removed by soot blowing.

Figure 4-28 shows the results of tests with a moving bed reactor and the ring type catalyst for flue gas from a coal-fired boiler. The gas contained about 30 mg/Nm^3 particulates after passing through an electrostatic precipitator. The total test period was 6000 hours. The NH_3/NO_x mole ratio was kept at 1.1 for over 5000 hours and then changed to 1.0. The reaction temperature was maintained at 350°C for over 5500 hours and then changed to between 280-350°C. Pressure drop of the gas through the reactor was about 70 mmH_2O initially. When it reached 90-130 mmH_2O, 20 to 100 percent of the catalyst was replaced to lower the pressure to 70-90 mmH_2O. NO_x removal efficiency was kept above 90 percent during the tests



Circled figures show times when SV and HN_3/NO mole ratio were changed.

1. SV 10,000 → 20,000 hr^{-1}
2. SV 10,000 → 15,000 hr^{-1}
3. SV 15,000 → 20,000 hr^{-1}
4. SV 6,200 → 4,500 hr^{-1}
5. SV 4.500 → 6,200 and the mole ratio 0.95 → 0.83

Figure 4-27. Test results for ring catalysts used on gas and oil fired boilers.

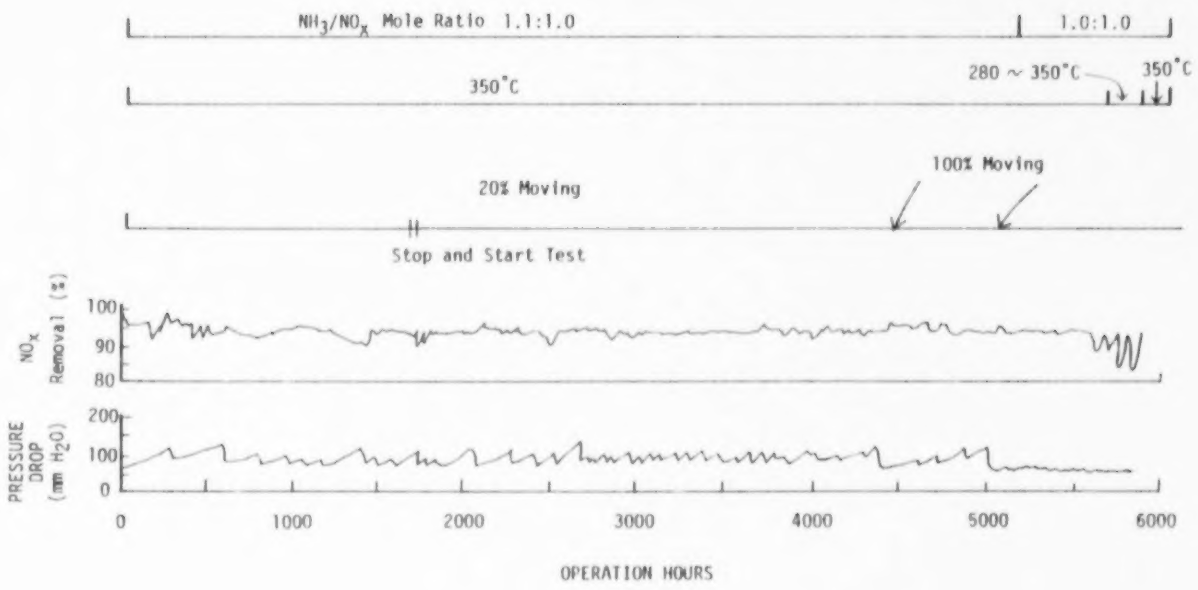


Figure 4-28. Tests of a moving bed reactor with a 2000 Nm^3/hr capacity for coal-fired boiler flue gas after a hot electrostatic precipitator.

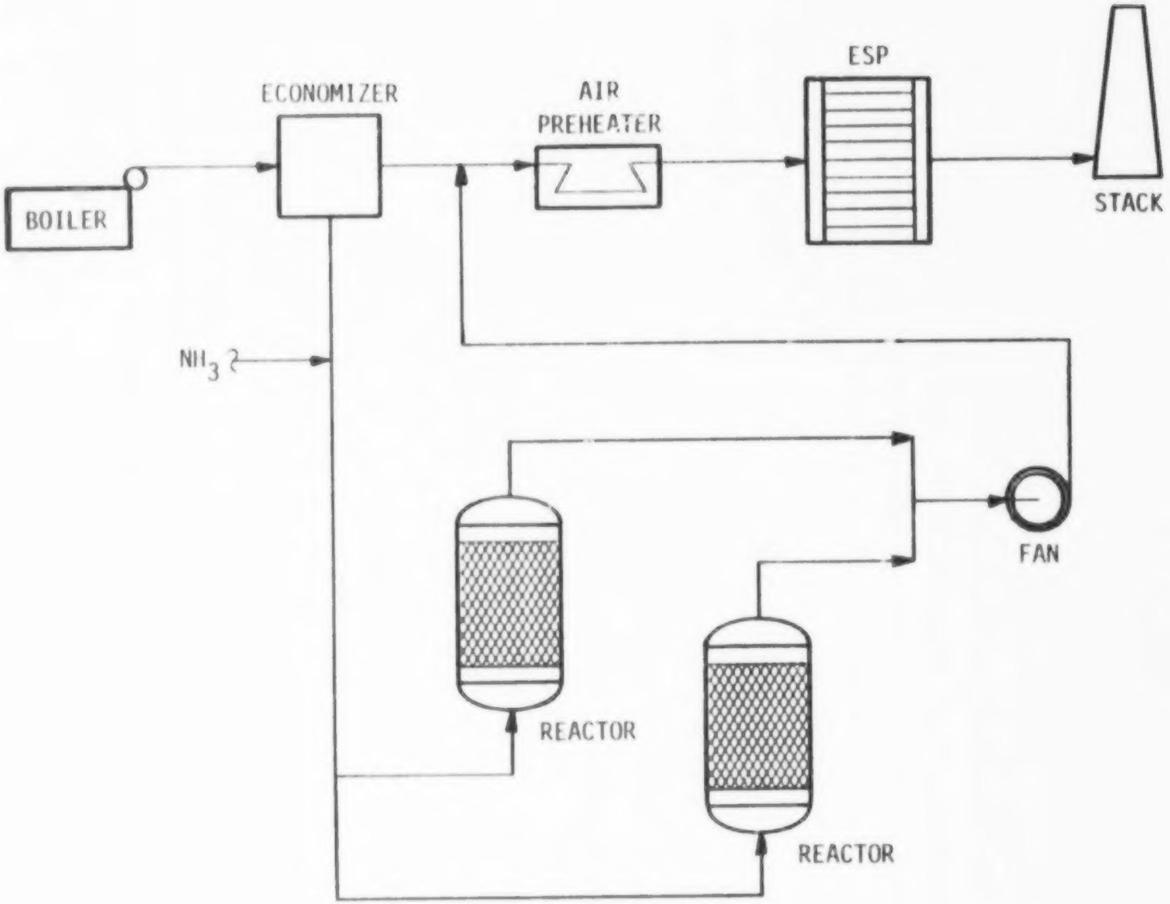
except when the temperature was lowered to 280°C. Efficiency dropped to 85 percent at the lowered temperature.

4.3.4 Kainan Plant, Kansai Electric

The plant treats 300,000 Nm^3/hr of flue gas which is one-fourth of the total gas from an existing 450 MW oil-fired utility boiler burning oil containing 0.2 percent sulfur. The gas leaving the boiler economizer contains about 100 ppm of SO_2, 2-3 ppm of SO_2, 100 ppm of NO_x and 20 mg/Nm^3 of particulates at 330-380°C. Ammonia diluted with air is injected in the flue gas and sent to a reactor with two compartments each with a capacity of treating 150,000 Nm^3/hr of the gas (Figure 4-29). For test, two different kinds of Raschig ring type catalysts, a high quality one and a low cost one, both with a size of about 15 mm, have been used. One of the compartments contains the high quality catalyst and the other contains the low cost catalyst. The bed depth is about 30 cm and the SV about 5700. The gas temperature fluctuates from 380°C at full load (450 MW) to 330°C at minimum load (150 MW).

An NH_3/NO_x mole ratio of 1.07 has been used to achieve an overall removal of 80 percent of NO_x with about 10 ppm of leak ammonia. It is estimated that over 90 percent NO_x removal efficiency is obtained at that mole ratio if the high quality catalyst is used in both beds.

The pressure drop of the SCR unit which has 40 mmH_2O initially went up to 165 mmH_2O after 11 months' continuous operation, when the boiler was subjected to scheduled shutdown for annual maintenance. The increased pressure drop did not upset operations because the booster fan (induced draft fan) installed for the SCR unit has a capacity of 200 mmH_2O. During the boiler shutdown period of one month, the catalyst was screened to remove particulates and then replaced in the beds.


ECONOMIZER
AIR PREHEATER
ESP
BOILER
STACK
NH_3
FAN
REACTOR
REACTOR

70-1333-1

Figure 4-29. Flowsheet of the Kainan SCR plant.

The SCR unit was connected to the boiler in 1977 during a two-month scheduled shutdown period for annual maintenance. Oil-fired boilers are normally shut down annually--for two months every other year and one month in between. Since the modification was made in a shutdown period, the boiler operation was not hindered.

4.3.5 Chita Plant, Chubu Electric

Chubu Electric installed full-scale SCR plants for two new LNG-fired boilers, each with a capacity of 700 MW. A flowsheet of the plant is shown in Figure 4-30. Flue gas (1,900,000 Nm^3/hr) from the economizer of the 700 MW boiler is injected with air-diluted ammonia and is sent to 2 parallel reactors. Each reactor, measuring 10.5 x 11.5 x 12.0 m, has four 11 cm-deep layers of pellet catalyst. The flue gas passes one of the layers. The SV is 20,000 hr^{-1}. The gas temperature ranges from 350°C at 700 MW load and 290°C at 250 MW load.

The inlet NO_x concentration is only about 35 ppm because of good combustion control. By adding 0.8 mole of NH_3 for each mole of NO_x, 80 percent of the NO_x is removed. NH_3 leakage is 5 ppm or below. The plants have been operated without trouble since start-up in April 1978.

4.3.7 Economics

The investment costs, including the initial charge for the catalyst, was 1.7 billion yen ($85 million) in 1978 for the two SCR plants (total 1400 MW) at Chita station and 1.2 billion yen ($60 million) in 1977 for the Kainan plant. The large difference in the cost per kilowatt--1210 yen ($6.05) at Chita and 10,670 yen ($53.35) at Kainan--is due to the following:

1) Chita has clean gas (SV 20,000 hr^{-1}) while Kainan has dirty gas.

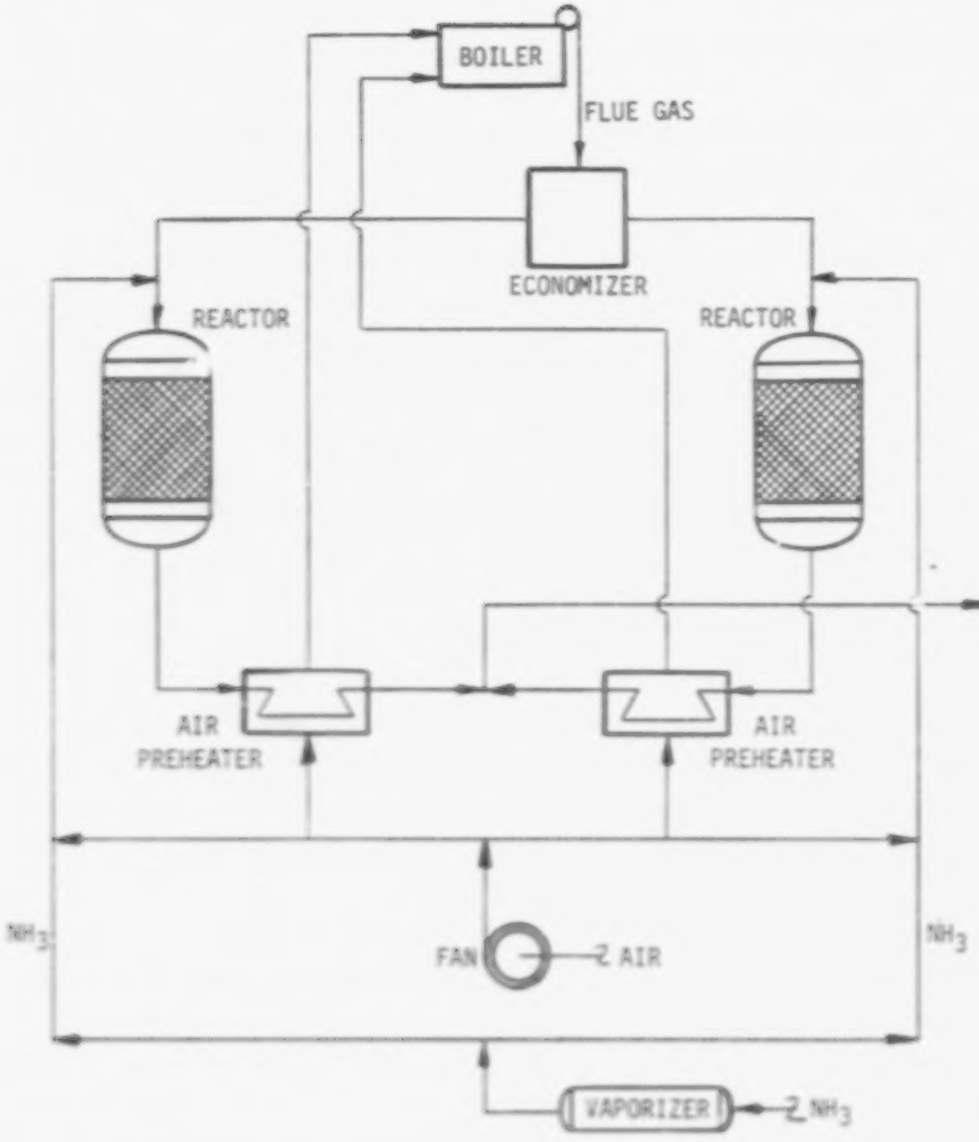

BOILER
FLUE GAS
ECONOMIZER
REACTOR
REACTOR
STACK
AIR PREHEATER
AIR PREHEATER
NH_3
NH_3
FAN
AIR
VAPORIZER
NH_3

Figure 4-30. Flowsheet of the Chita SCR plant.

2) Chita has a new boiler while Kainan has an existing boiler.

3) Chita is much larger.

4) Kainan plant has various equipment for the operation of the test equipment.

It is roughly estimated that the investment cost for a full-scale SCR plant for an existing 450 MW oil-fired boiler is about 3 billion yen (6700 yen/kW or $34/kW). The cost should be considerably lower for a new boiler. The catalyst life is estimated at 2 years for dirty gas and longer for clean gas.

Operation of SCR plants is simple and is controlled from inside the boiler control room.

4.3.8 Evaluation

Hitachi's ring type catalyst is not only highly reactive and SO_x-resistant but is also less vulnerable to dust plugging and strong enough to withstand use in a moving bed. The smooth operation of the commercial and prototype plants shows the reliability of the Hitachi process.

The plate catalyst may be most suitable for preventing particulate plugging. Compared with metallic honeycombs produced by chemical treatment of the surface of a metallic alloy, larger varieties of compositions of plate catalysts may be produced by cementing catalyst powder on metal plate. Although 90 percent NO_x removal is achieved with the plates, they may be better suited for moderate NO_x removal efficiency, *e.g.*, 70-80 percent for new boilers. For existing boilers, 30-50 percent removal may be achieved simply by placing a small amount of the catalyst plates in the duct between the boiler economizer and the air preheater, without installing a reactor or fan and by using less than 0.7 mole NH_3 for each mole of NO_x to minimize the NH_3 leakage. A combination of combustion modification and the simple type SCR with an NO_x removal efficiency of 50-70 percent may be one of the best ways for NO_x abatement for existing boilers.

Hitachi's pilot plant test with flue gas from a coal-fired boiler has shown that by reducing the particulates content to about 200 mg/Nm^3 with a hot electrostatic precipitator, a moving bed reactor with the ring catalyst works well. Further improvement of plate catalysts, however, may make them advantageous over a moving bed reactor.

Hitachi is going to construct a commercial SCR plant with plate catalyst for a new coal-fired boiler of Hokkaido Electric (Table 1-14), and plans to use a hot electrostatic precipitator because it can efficiently remove the fly ash from the domestic low sulfur coal to be used for the boiler.

When a hot electrostatic precipitator is used, the prevention of ammonium bisulfate deposits in the air preheater is important. Experience indicates that the sweeping effect of a large amount of fly ash in coal-fired flue gas helps to reduce the deposits.

4.4 JGC PROCESS (PARANOX PROCESS)

4.4.1 Introduction

JGC Corporation (former Japan Gasoline Co.), one of Japan's largest engineering and plant construction companies, constructed a Shell process flue gas desulfurization unit at Yokkaichi for Showa Yokkaichi Seikiyu (SYS). They used the parallel passage reactor developed by Shell. JGC has produced SCR catalysts and applied them to the reactor for SCR, and constructed two relatively small commercial SCR units for Kashima Oil and Fuji Oil to treat flue gas from heavy-oil burning gas. In addition, JGC has tested in a pilot plant the use of a newly developed low-temperature catalyst for the treatment of flue gas from an iron-ore sintering machine.

Recently JGC constructed a large test plant for Nippon Steel to treat flue gas from a coke oven.

4.4.2 Parallel Passage Reactor

A parallel passage reactor, developed to treat dust-rich gas without particulates clogging, has the following structure (Figure 4-31):

1) A thin rectangular box made of metallic gauze is filled with the catalyst. This box is called an "envelope" and forms the catalyst layer.

2) These envelopes are placed in parallel at narrow intervals. The flue gas flows through the interval space along the surface of the envelopes. This interval space is called the "gas channel."

3) For ease of handling, a set of envelopes is placed in a large square box called a "unit cell." The top and bottom are open so that the flue gas can flow up and down through the box.

4) The unit cells are stacked in a reactor shell to make a Parallel Passage Reactor. Flue gas can go through the reactor either upward or downward.

Since the gas passes through the gas channel parallel to the catalyst layers, dust plugging is avoided, except that a minor deposit of dust on the gauze can occur. JGC has developed a "sand blast" system to remove the deposit.

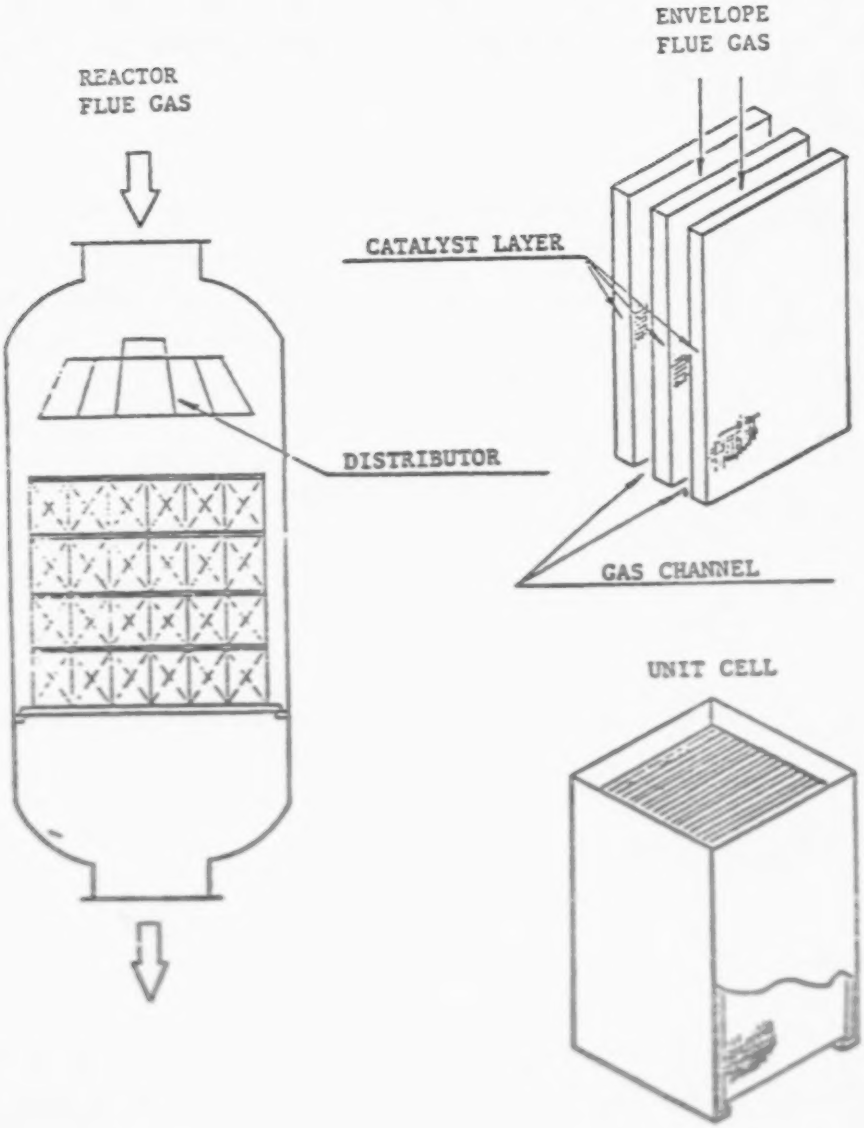

ENVELOPE
FLUE GAS
REACTOR
FLUE GAS
CATALYST LAYER
DISTRIBUTOR
GAS CHANNEL
UNIT CELL

Figure 4-31. Construction of a parallel passage reactor.

4.4.3 Catalyst

The catalyst is a small cylinder, 1 mm in diameter and 3-5 mm in length. Great mechanical strength is not needed because the catalyst is packed in an envelope. Therefore, the catalyst can be porous to provide high reactivity.

Figures 4-32 - 4-34 show the NO_x removal efficiencies in laboratory tests with a high-temperature catalyst JP 102 and a low-temperature catalyst JP 501. For the tests, the catalysts were packed in an ordinary packed bed (not parallel passage) through which gas was passed. Since the catalysts are small and reactive, high efficiency was obtained at a large SV of 20,000. The catalyst JP 102 is active above 350°C and is suitable for boiler flue gas, while JP 501 is active even at 250°C and suits low temperature gases.

Figure 4-34 indicates that the activity of the low-temperature catalyst is stable at 300°C but is lowered at 250°C and 230°C. The decrease in activity is caused by the deposit of ammonium bisulfate on the catalyst below 270°C. By heating the contaminated catalyst above 350°C, ammonium bisulfate is removed by decomposition and catalyst activity is restored.

4.4.4 Commercial Plants[2]

Design and operation data of two commercial plants are listed in Table 4-8.

The first commercial plant at Kashima Refinery (Figure 4-35) was completed in November 1975 and can treat 50,000 Nm^3/hr of flue gas from a heating furnace burning heavy oil containing 90-130 ppm of NO_x, 310-680 ppm of SO_x, and 20-40 mg/Nm^3 of particulates. Flue gas at 215-225°C is heated by an inline heater to 380-395°C, injected with ammonia at an NH_3/NO_x mole ratio of 1.0-1.2, and introduced into a parallel passage

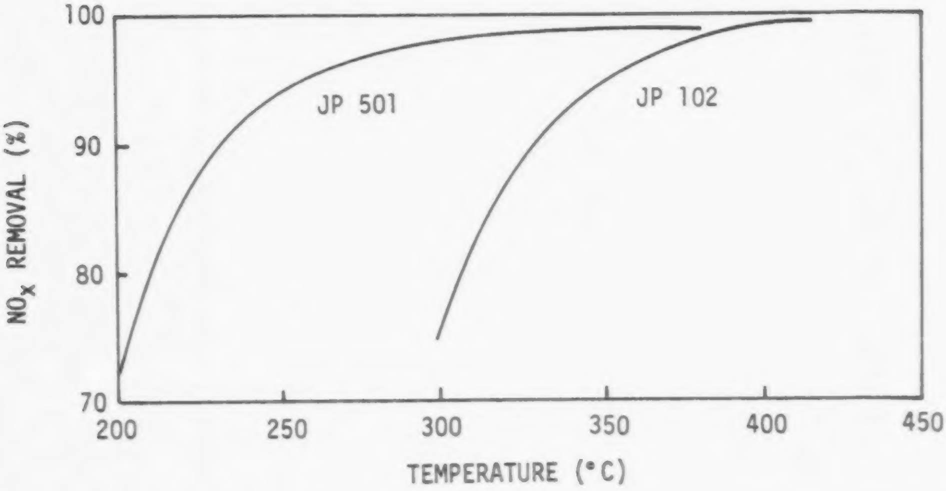


Figure 4-32. The effect of temperature on the activities of catalysts JP 501 and JP 102 (NO, 200 ppm; NH_3, 240 ppm; O_2, 3 percent; H_2O, 10 percent; SV, 20,000 hr^{-1}).

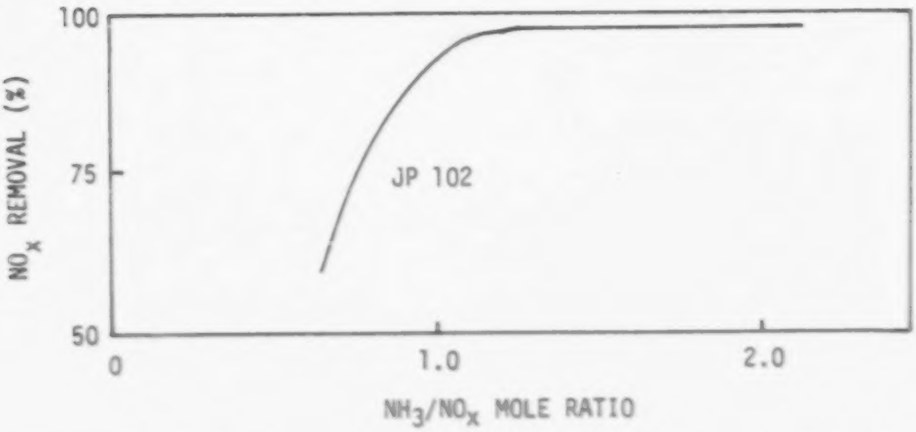


Figure 4-33. The effect of NH_3/NO mole ratio on the activities of catalysts JP 501 and JP 102 (380°C; SV, 20,000 hr^{-1}; NO, 200 ppm; SO_2, 1500 ppm; O_2, 3 percent; N_2, 0 percent).

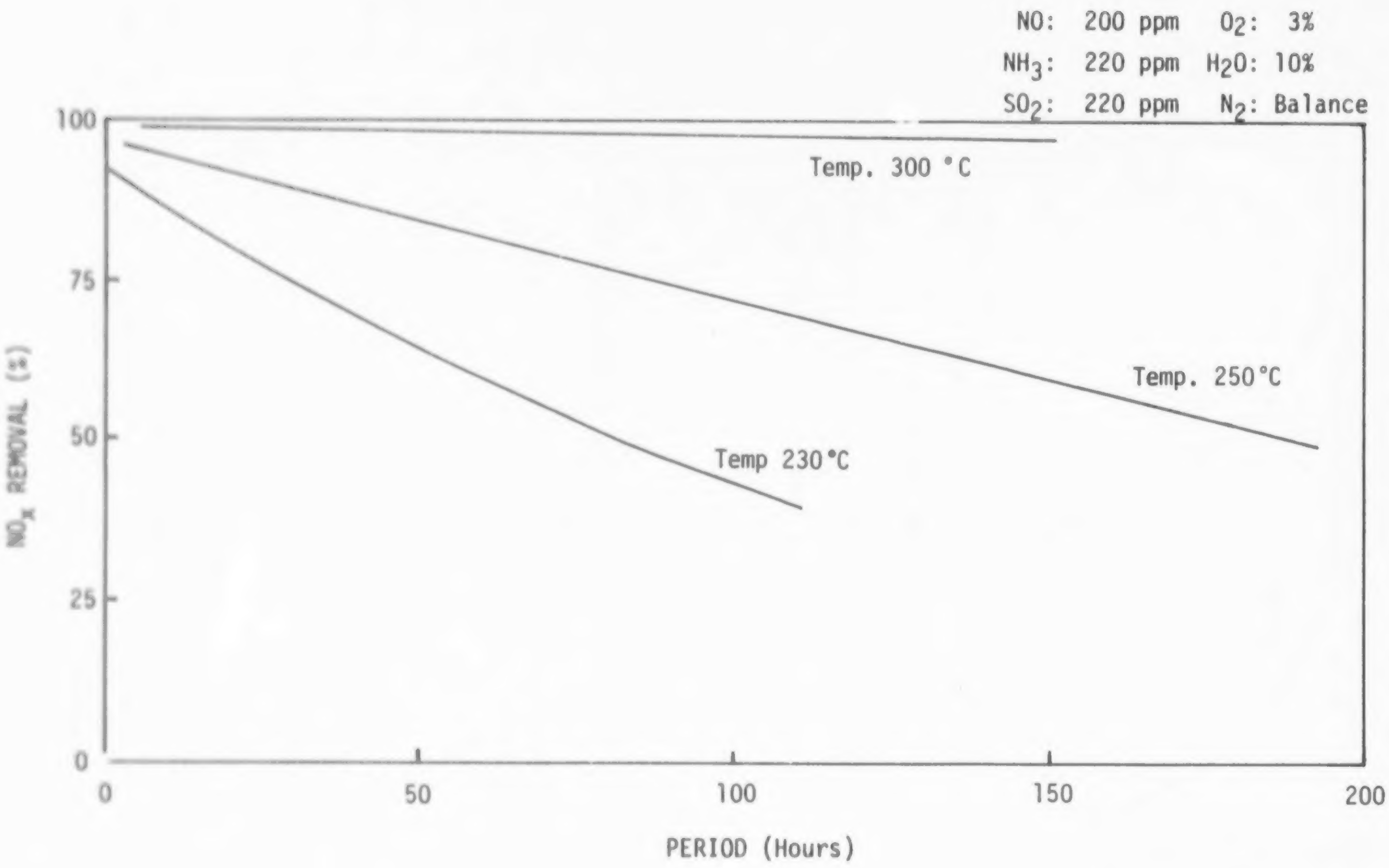


Figure 4-34. The change in NO_x removal efficiency with reaction temperature and time for catalyst JP 501.

TABLE 4-8. DESIGN AND OPERATION DATA OF COMMERCIAL SCR PLANTS (JGC PROCESS)

	Kashima Plant, Kashima Oil (Heating Furnace Flue Gas)		Chiba Plant, Fuji Oil (FCC CO Boiler Flue Gas)	
	Design	Operation	Design	Operation
Flue Gas				
Volume (Nm^3/hr)	50,000	49,000-51,000	70,000	78,000-81,000
Temperature (°C)	220-250	215-225	380-420	365-410
NO (ppm)	60-250	90-130	180	160-220
SO_x (ppm)	370-850	310-680	630	340-660
Particulates (mg/Nm^3)	Below 50	20-40	100	60-70
O_2 (percent)	5-11	7-11	3	2
H_2O (percent)	11-16		10	13
Reaction Temperature	380-420	380-395	380-420	385-405
NH_3/NO_x Mole Ratio	1.2	1.0-1.2	1.2	1.0-1.2
Space Velocity (hr^{-1})	4000	4000	4000	4000
NO_x Removal Efficiency (percent)	Above 90	95-98	90	93-96
Pressure Drop in Reactor (mmH_2O)	200	140-180	160	115-125

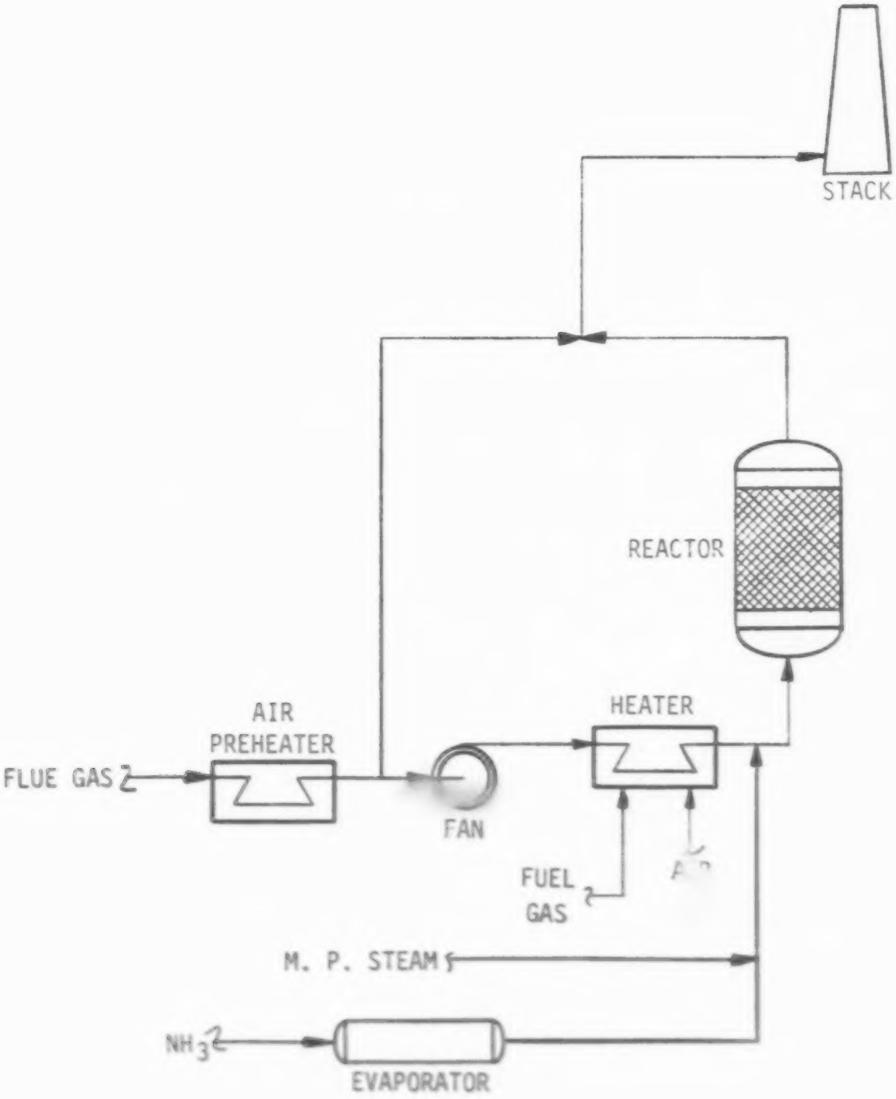

STACK
REACTOR
AIR PREHEATER
FLUE GAS
FAN
HEATER
FUEL GAS
AIR
M. P. STEAM
NH_3
EVAPORATOR

Figure 4-35. Paranox process for Kashima Oil, 50,000 Nm^3/hr.

reactor to remove 95-98 percent of NO_x at an SV or 4000 hr^{-1}. The ammonia concentration of the reactor effluent is about 10 ppm.

The plant was operated continuously without problems for about 16 months but has been inoperative most of the time since then. Because of the low operating load, the total emission of NO_x of the refinery has decreased so that denitrification has become unnecessary.

Another commercial plant was constructed for Fuji Oil at Chiba (Sodegaura) Refinery (Figure 4-36) and began operation in July 1976. The flue gas is discharged from a boiler economizer at 360-410°C and has the composition shown in Table 4-8. A gas-fired heater with a capacity of 3.6×10^6 kcal/hr has been installed but is used only for limited periods because the gas temperature is close to the desired range of 380-420°C.

Ammonia is diluted with steam and injected into the gas. The unit has an open-bypass system with a blower with a capacity of 80,000 Nm^3/hr. Usually, a portion of the gas leaving the reactor is circulated through the bypass and introduced into the reactor together with the gas from the boiler. The total gas volume and the pressure drop in the reactor are kept almost constant so boiler operation is not adversely affected regardless of the fluctuation of the gas volume from the boiler. By using 1.0-1.2 moles of NH_3 for each mole of NO_x, 93-96 percent of the NO_x is removed with leak NH_3 (NH_3 in the reactor outlet gas) ranging from 50 to 30 ppm according to the mole ratio.

The unit was operated without serious problem for nearly 2 years. A small amount of particulates tends to adhere to the metal gauze of the elements and the unit has a sand blast system to remove the particulates. The sand blast system, however, has seldom been used. The catalyst itself has been kept relatively clean and the life is estimated at over 2 years. The floor space occupied by the SCR unit is about 250 m^2. The plant is not operated currently for the same reasons as with the above Kashima plant.

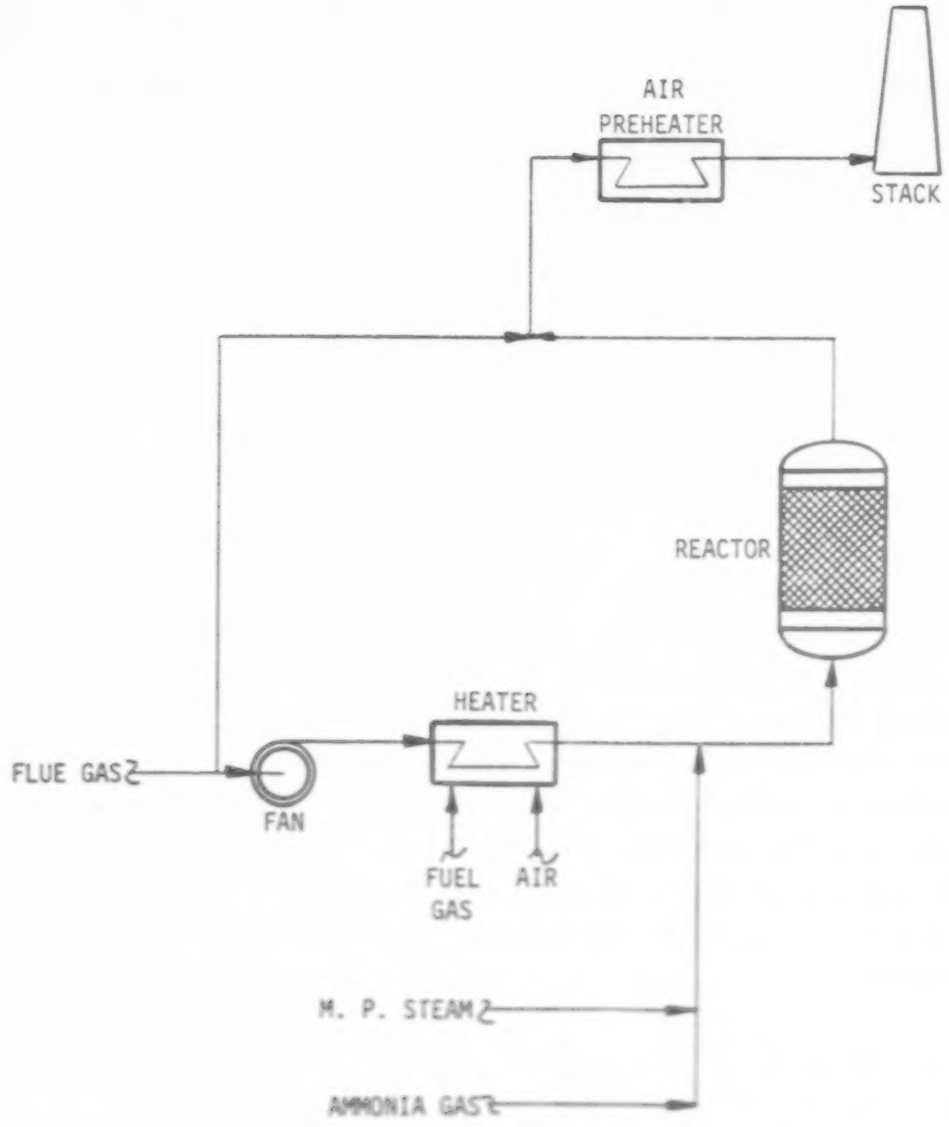

AIR
PREHEATER
STACK
REACTOR
HEATER
FLUE GAS
FAN
FUEL
GAS
AIR
M. P. STEAM
AMMONIA GAS

Figure 4-36. Paranox process for Fuji Oil, 70,000 Nm^3/hr.

4.4.5. Pilot Plant Tests with Sintering Machine Flue Gas[3]

JGC has conducted pilot plant tests at the Nagoya Works, Nippon Steel, sponsored by the NO_x Fund of the Steel Federation. The pilot plant can treat 2000 Nm^3/hr of flue gas from an iron-ore sintering machine with the composition shown in Table 4-9. The gas contains less than 250 mg/Nm^3 particulates before an electrostatic precipitator (ESP) and less than 50 mg/Nm^3 after the ESP. The composition and size distribution of the particulates are shown in Table 4-10.

TABLE 4-9. COMPOSITION OF THE GAS FROM THE IRON-ORE SINTERING MACHINE AT NAGOYA WORKS, NIPPON STEEL

NO_x	150-250 ppm	SO_x	Below 200 ppm
O_2	15-17 percent	CO_2	5-6 percent
H_2O	10-12 percent	Particulates	Below 250 mg/Nm^3

TABLE 4-10. COMPOSITION AND SIZE OF THE PARTICULATES IN THE GAS FROM THE IRON-ORE SINTERING MACHINE AT NAGOYA WORKS, NIPPON STEEL

Fe (as Fe_2O_3)	77-86 percent	C	About 5 percent
SiO_2	4-7 percent	Al_2O_3	1-3 percent
CaO	4-8 percent		

Minor Components - Mg, Mn, Zn, Pb, K, Na, etc.

Size (μ)	Distribution (percent)	
	Before ESP	After ESP
Below 10	1	6
10-60	4	9
60-100	15	40
Above 100	80	45

High and low temperature catalysts are used for both the gases before and after the ESP as shown in Table 4-11.

TABLE 4-11. CONDITIONS OF JGC TESTING AT NAGOYA WORKS, NIPPON STEEL

Test No.	Test Hours	Gas Obtained	Catalyst Type	Reaction Temp. (°C)	SV (hr^{-1})	NH_3/NO_x Mole Ratio
1	1500	After ESP	High Temp.	390	3150	1.2-1.5
2	700	Before ESP	High Temp.	390	3150	1.2-1.5
3	1200	After ESP	Low Temp.	300	3620	1.2-1.5
4	6700	Before ESP	Low Temp.	290-300	3620	1.2-1.5

Since the flue gas was at about 160°C, the gas was heated to the desired temperature by a heat exchanger and a heater. The results of tests by No. 1 - No. 3 are shown in Figures 4-37 - 4-39.

During tests No. 1 and No. 2, there were short interruptions due to the shutdown of the sintering machine. Tests No. 3 and No. 4 were carried out continuously for 1200 and 6700 hours, respectively. In tests No. 1 and No. 2, about 95 percent of the NO_x was removed at a pressure drop of 100-150 mmH_2O. The pressure drop did not increase in test No. 1, but it did increase about 10 mmH_2O about 700 hours into test No. 2. In test No. 3, NO_x removal efficiency decreased from 98 to 96 percent and the pressure drop increased from 105-110 to 120-130 mmH_2O after 1200 hours.

In test No. 4, 95-96 percent of the NO_x was removed at 300°C, while at 290°C the initial NO_x removal efficiency of 93 percent decreased to 90 percent after 1200 hours. By heating up the flue gas to 380°C for two hours, the NO_x removal efficiency recovered to 93 percent. The pressure drop increased from 130 to 180 mmH_2O after 5300 hours and stayed at 180 mmH_2O. The plant operation was trouble-free.

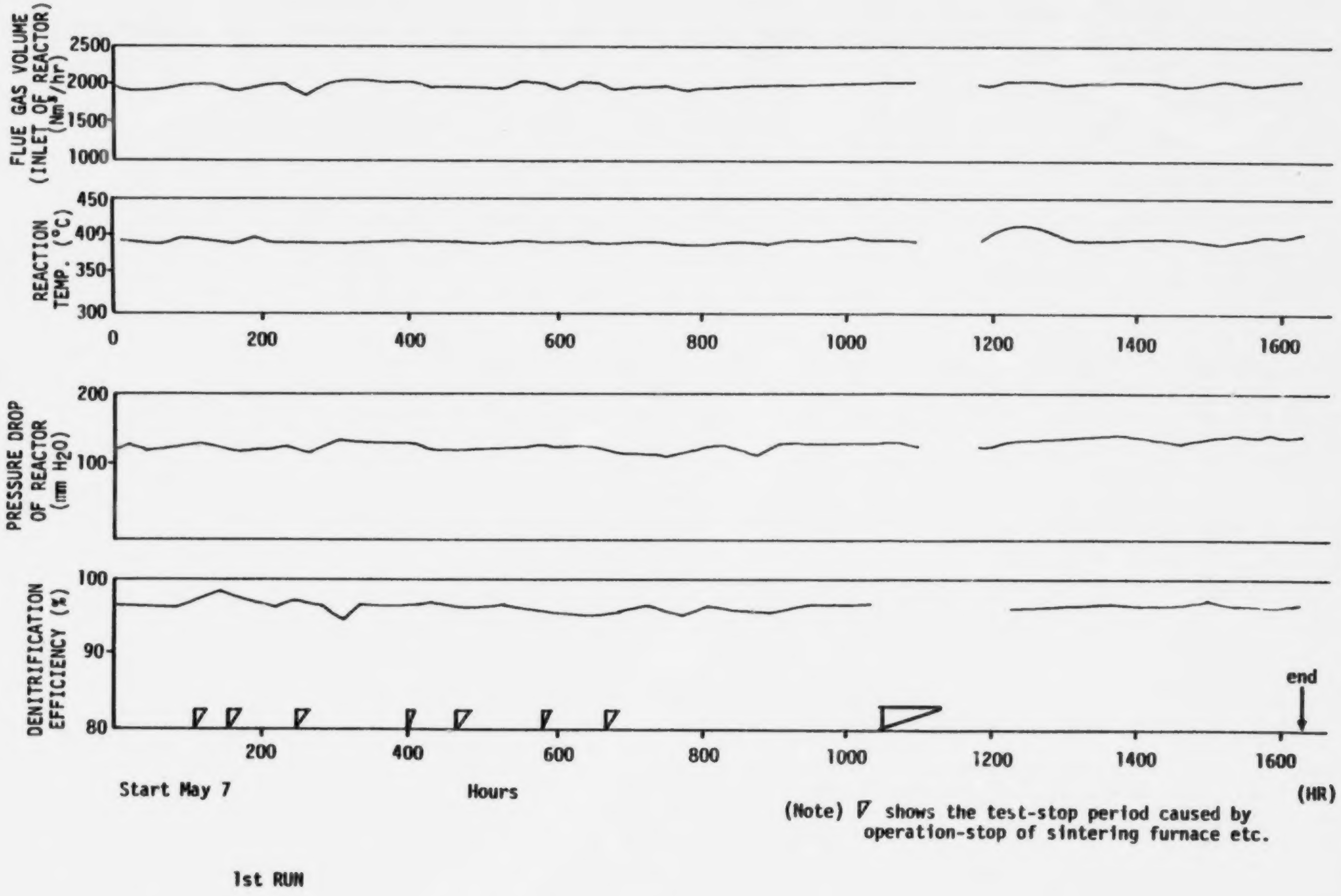


Figure 4-37. Results of JGC testing of a high temperature catalyst at Nagoya Works, Nippon Steel, for flue gas after an electrostatic precipitator.

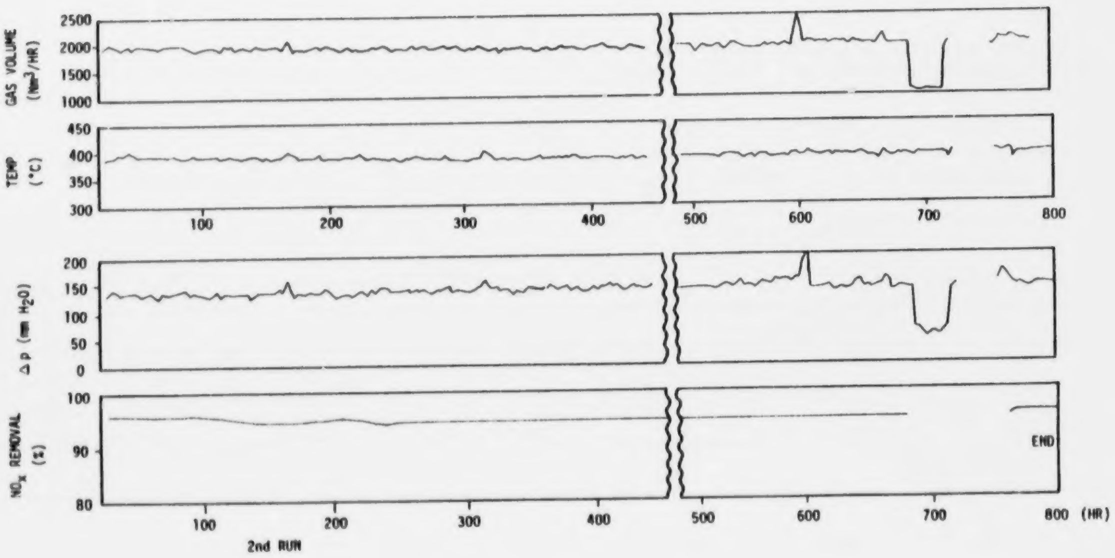


Figure 4-38. Results of JGC testing of a high temperature catalyst at Nagoya Works, Nippon Steel, for flue gas before an electrostatic precipitator.

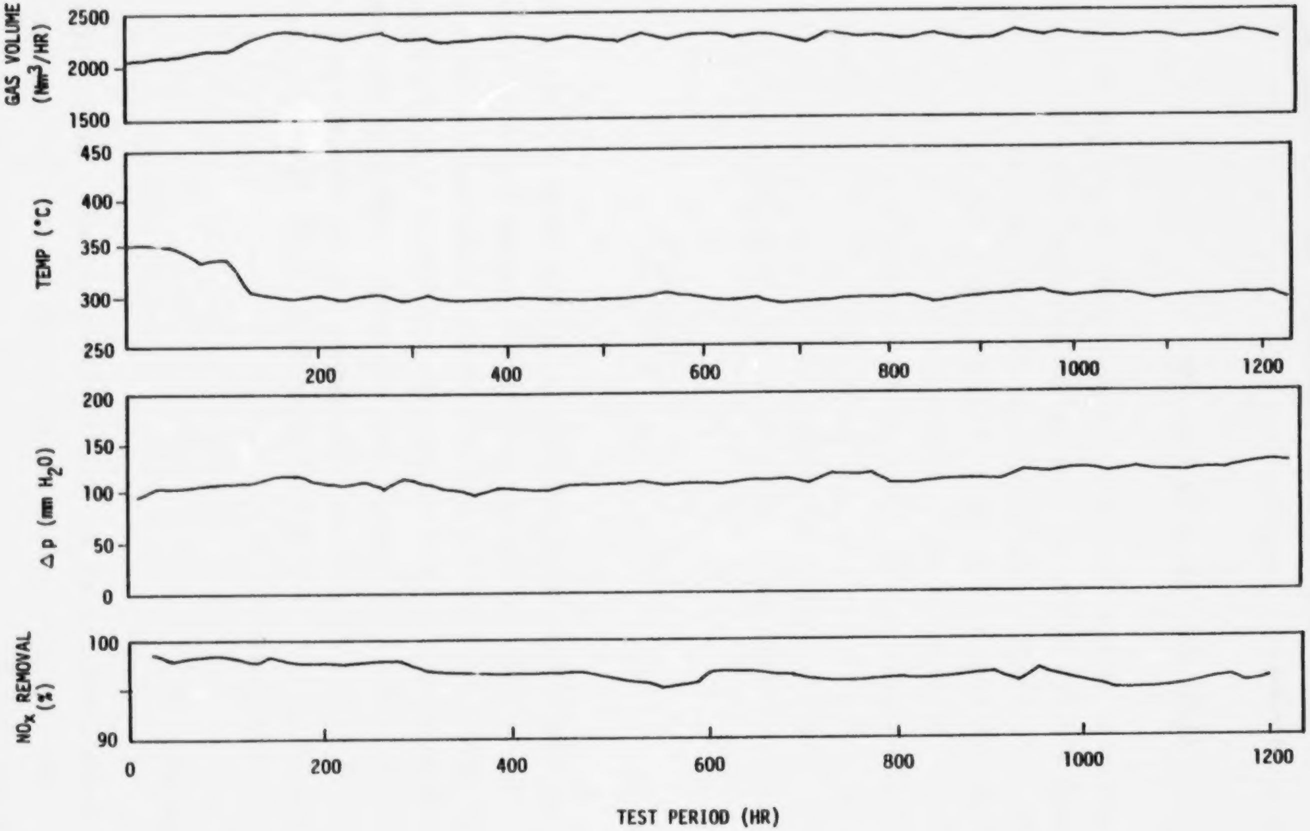


Figure 4-39. Results of the third run of JGC testing of a low temperature catalyst at Nagoya Works, Nippon Steel, for flue gas after an electrostatic precipitator.

A considerable amount of dust from the sintering machine and some ammonium bisulfate deposited in the heat exchanger but they could be removed by soot blowing.

4.4.6 Prototype Plant for Coke Oven Flue Gas

JGC constructed at the Kimitsu Works of Nippon Steel a prototype plant which can treat 150,000 Nm^3/hr of flue gas from a coke oven containing about 200 ppm of NO_x and 50 ppm of SO_x. The gas at about 200°C is treated by a low-temperature catalyst in a parallel passage reactor at an SV of 4000. The NO_x removal efficiency is about 95 percent initially and decreases to about 90 percent in about a week due to the deposit of ammonium bisulfate on the catalyst. The flue gas is then heated above 350°C by a heater to decompose and remove the ammonium bisulfate on the catalyst and to regain the high NO_x removal efficiency. Details of the plant operation have not been disclosed yet.

4.4.7 Economics

JGC claims that the investment cost for the SCR plant for flue gas from a 33-150 MW oil-fired boiler is 7500-15,000 yen/kW ($37.50-$75/kW) excluding site preparation and the control room. Actually, the Chiba plant, Fuji Oil (23 MW equivalent), cost 490 million yen ($2.45 million) including the 40 million yen ($200,000) initial charge for the catalyst. The catalyst life is estimated at 2 years. Power requirement for the fan of the plant is 250 kW. Operating cost is reported to be 8200 yen/hr ($41/hr) including ammonia and electrical power.

4.4.8 Evaluation

The catalysts developed by JGC are SO_x-resistant and highly efficient. The commercial and test plants constructed by JGC for SCR have had little problem achieving over 90 percent NO_x removal. JGC appears to have established know-how for SCR application of the parallel passage reactor originally developed by Shell. The process is one of the most reliable processes commercially proven for dirty gas treatment and may be applicable also for flue gas from a coal-fired boiler without prior fly ash removal.

On the other hand, the parallel passage reactor has the following drawbacks: 1) relatively large pressure drop, 2) relatively small SV, and 3) relatively high cost.

Moving bed reactors have also been used for treating flue gas from oil-fired boilers. Tubular and honeycomb type catalysts are beginning to be used for boiler flue gas and gas with higher particulate content. Further comparison of the operation of the parallel passage reactor with the other types of catalysts should be made in the future.

The low-temperature catalyst developed by JGC may be more economical for low-temperature gases than the conventional SCR catalysts which are active at 300-400°C, although intermittent gas heating to 350°C is needed to remove ammonium bisulfate.

4.5 MITSUI ENGINEERING AND SHIPBUILDING PROCESS

4.5.1 Introduction

Mitsui Engineering and Shipbuilding Co. (formerly Mitsui Shipbuilding Co.), one of the largest engineering and shipbuilding companies in Japan, has studied SCR in cooperation with Mitsui Petrochemical Co., and constructed a commercial plant for both Mitsui Petrochemical and Ukishima Petrochemical. Both use a fixed bed reactor.

The first plant, built for Mitsui Petrochemical in Chiba, can treat 220,000 Nm^3/hr of flue gas from a boiler burning a sulfur-free oil by using an alumina-based catalyst placed in a special type of parallel flow reactor. The second plant, for Ukishima Petrochemical in Chiba, uses a titania-based tubular catalyst and can treat 220,000 Nm^3/hr of flue gas from boilers burning heavy oil.

Mitsui has made extensive tests on tubular type catalysts at a pilot plant at Tamashima Power Station, Chugoku Electric.

4.5.2 Chiba Plant, Mitsui Petrochemical

A flowsheet of the Chiba Plant of Mitsui Petrochemical is shown in Figure 4-40. The plant was installed for an existing boiler which discharges flue gas through an air preheater and an electrostatic precipitator at 150°C. The gas is heated by a gas-gas heat exchanger and an oil-fired heater to 350°C. The operation parameters are shown in Table 4-12. Over 90 percent of the NO_x in the gas is removed at an NH_3/NO_x mole ratio of 1 and an SV of 2500 hr^{-1}. The gas contains virtually no SO_x with a small amount of particulates. Plant operation was trouble-free, but is currently stopped because of the high cost of fuel used for gas heating.

4.5.3 Chiba Plant, Ukishima Petrochemical

The Chiba Plant of Ukishima Petrochemical began operation in July 1977. It can treat 220,000 Nm^3/hr of flue gas from a new industrial boiler burning a 0.6 percent sulfur oil. A flowsheet is shown in Figure 4-41. Operation parameters are shown in Table 4-12. The plant has no bypass. The flue gas from the boiler contains 150 ppm NO_x, about 300 ppm SO_x, and 100-150 mg/Nm^3 particulates. This gas at 350-400°C is injected with ammonia and is introduced into a reactor packed with a tubular catalyst. The catalyst, based on TiO_2, is resistant to SO_2 and SO_3 and has a 35 mm outer diameter, 20 mm inner diameter, and 1000 mm length. The catalyst is packed in a 1 m x 1 m x 1 m cubic container as shown in Figure 4-42. The reactor has 3 layers of containers; total packed height is 3 meters.

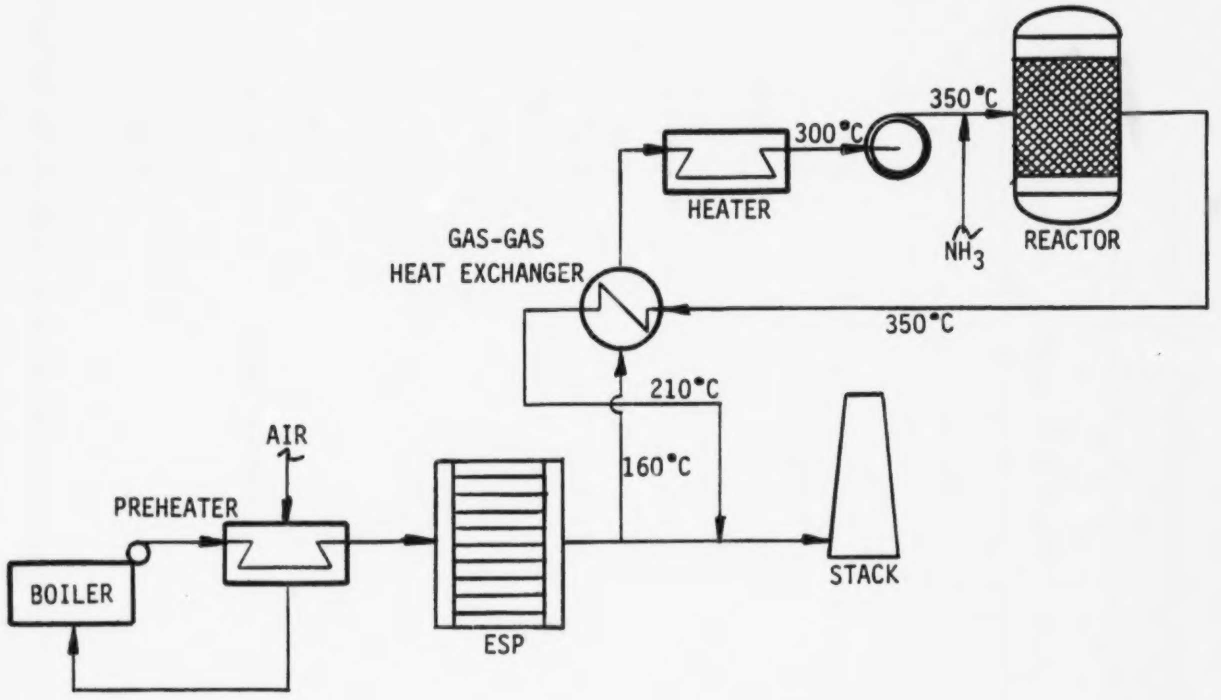

GAS-GAS
HEAT EXCHANGER
HEATER
300°C
350°C
NH_3
REACTOR
350°C
210°C
160°C
AIR
PREHEATER
BOILER
ESP
STACK

Figure 4-40. Flowsheet of Chiba Plant, Mitsui Petrochemical.

TABLE 4-12. OPERATING PARAMETERS OF MITSUI ENGINEERING & SHIPBUILDING CO. SCR PLANTS

	Mitsui Petrochemical Co.	Ukishima Petrochemical Co.
Capacity (Nm^3/hr)	200,000	220,000
Gas Composition		
NO_x (ppm)	190	150
SO_x (ppm)	None	300
Particulates (mg/Nm^3)	20-50	100-150
Catalyst and Reactor		
Catalyst Carrier	Al_2O_3	TiO_2
Catalyst Shape	Granule	Tube
SV (hr^{-1})	2600	4000
Temperature (°C)	350	350-400
NH_3/NO_x Mole Ratio	1.0	1.0
NO_x Removal (percent)	90	90
Total Pressure Drop (mmH_2O)		130
Leak NH_3 (ppm)		Below 10
Operation Start	October 1975	July 1977
Plant Cost (10^6 yen)		260
Denitrification Cost (yen/kWhr)*		0.33

* Including 7 years depreciation.

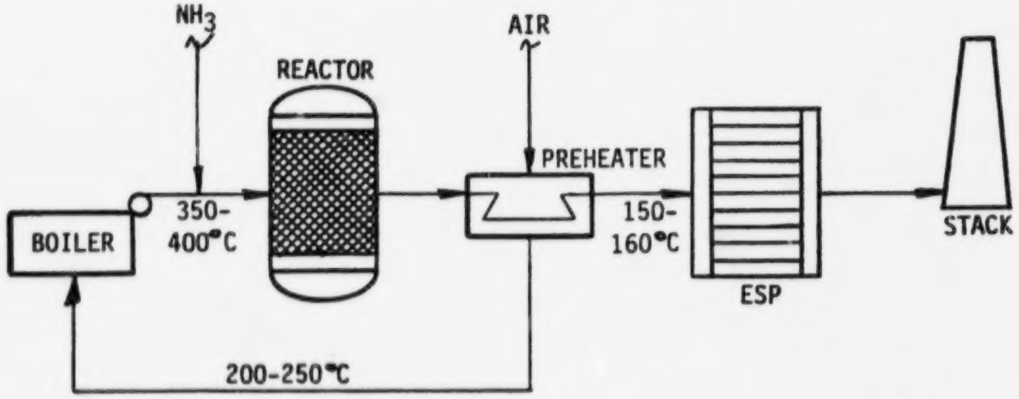

NH$_3$
REACTOR
AIR
PREHEATER
BOILER
350-
400°C
150-
160°C
ESP
STACK
200-250°C

Figure 4-41. Flowsheet of Chiba Plant, Ukishima Petrochemical.

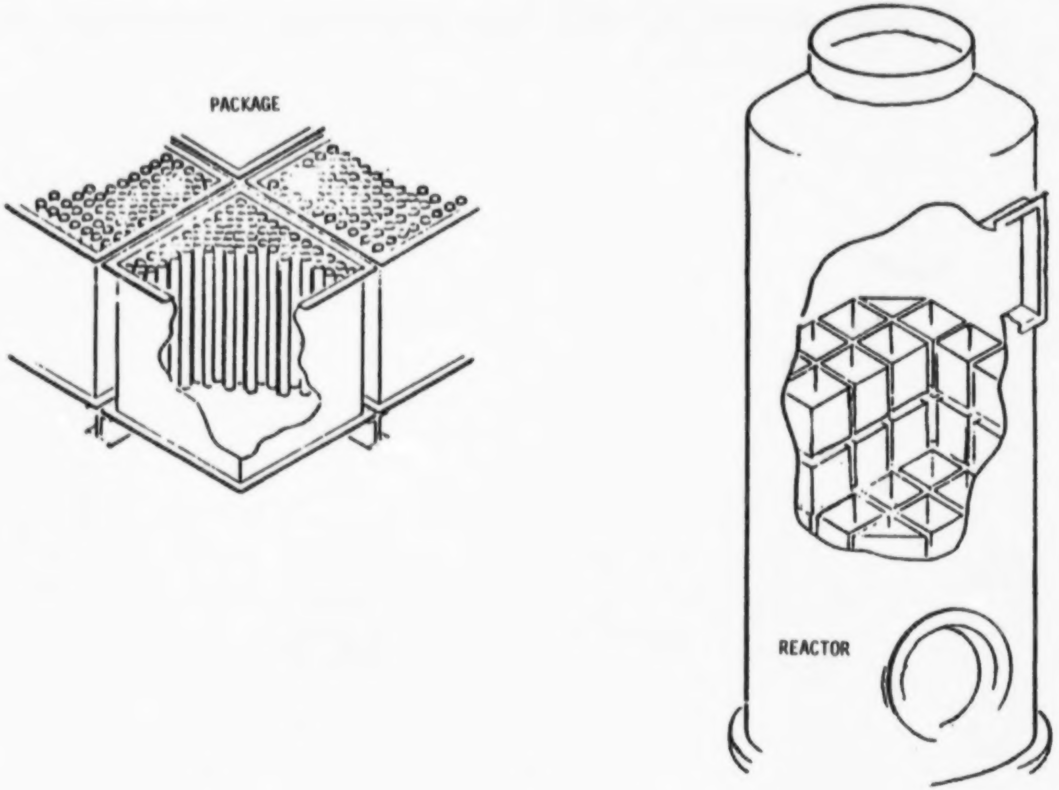

PACKAGE
REACTOR

Figure 4-42. Structure of a reactor with a tubular catalyst.

The superficial gas space velocity in the reactor is 7-8 meters with an actual gas velocity of 10-12 meters through the catalyst. About 90 percent of the NO_x can be removed by using 1 mole of ammonia for each mole of NO_x. The ammonia leakage is kept below 10 ppm. The pressure drop through the system is 130 mmH_2O, including 100 mm for the reactor and 30 mm for the ducts.

To cope with the drop of the gas temperature at reduced load, a system has been installed to bypass a portion of the hot gas before passing through the economizer.

The boiler supports an ethylene plant and has been frequently shut down due to the oversupply of ethylene. The SCR plant operation has been trouble-free except that ammonium bisulfate tends to deposit in the air preheater (Ljungstrom type). To cope with the problem, NH_3 concentration at the reactor outlet is maintained below 5 ppm by using a little less than 1 mole of ammonia for each mole of NO_x, a heating element with a simple element is used, and steam blowing has been applied. Two steam nozzles, each with a capacity of 1 ton/hr of steam of over 10 kg/cm^2 pressure, have been used intermittently. The steam consumption is equivalent to 0.3 percent of the steam generated by the boiler.

4.5.4 Tests on Tubular Catalysts

Mitsui Engineering has extensively tested tubular catalysts at a pilot plant.

One of the most important findings was that a much higher NO_x removal ratio and a smaller pressure drop were obtained by separate packing of the catalyst (Figure 4-43, B) than by contact packing (Figure 4-43, A) as shown in Figure 4-44. With contact packing, most of the gas passes inside the tubes where catalyst surface area is much smaller than outside the tubes. Tests have shown that best results (optimum efficiency) are obtained when the tubes are arranged in a separate position so that the ratio of gas

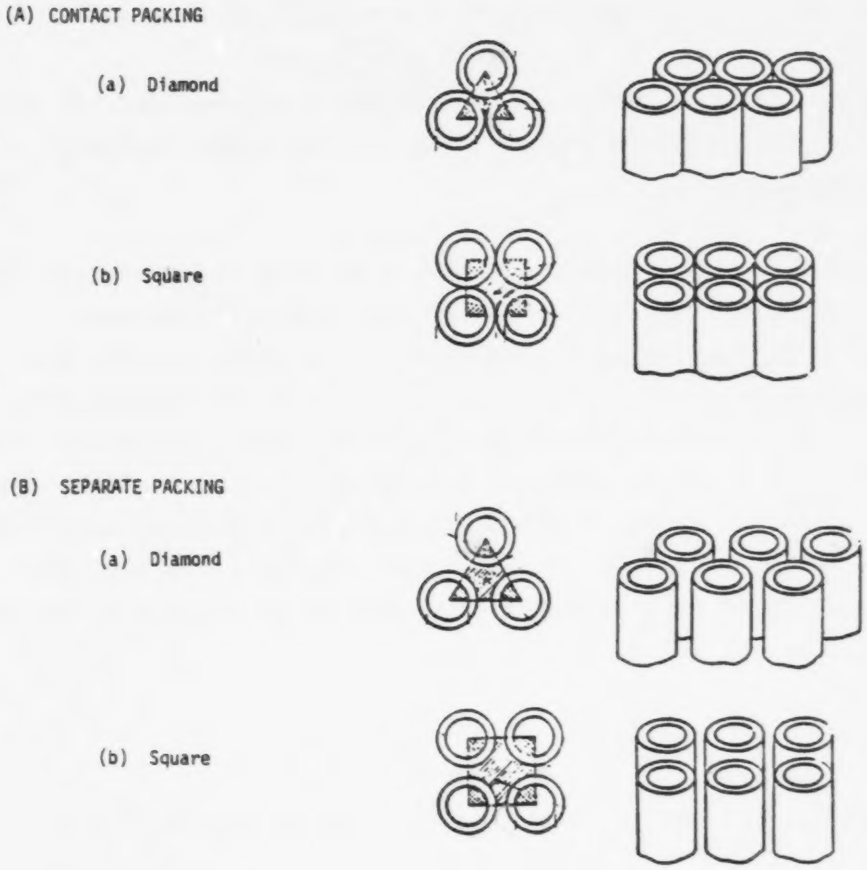

(A) CONTACT PACKING
(a) Diamond
(b) Square
(B) SEPARATE PACKING
(a) Diamond
(b) Square

Figure 4-43. Methods for packing of tubular catalysts.

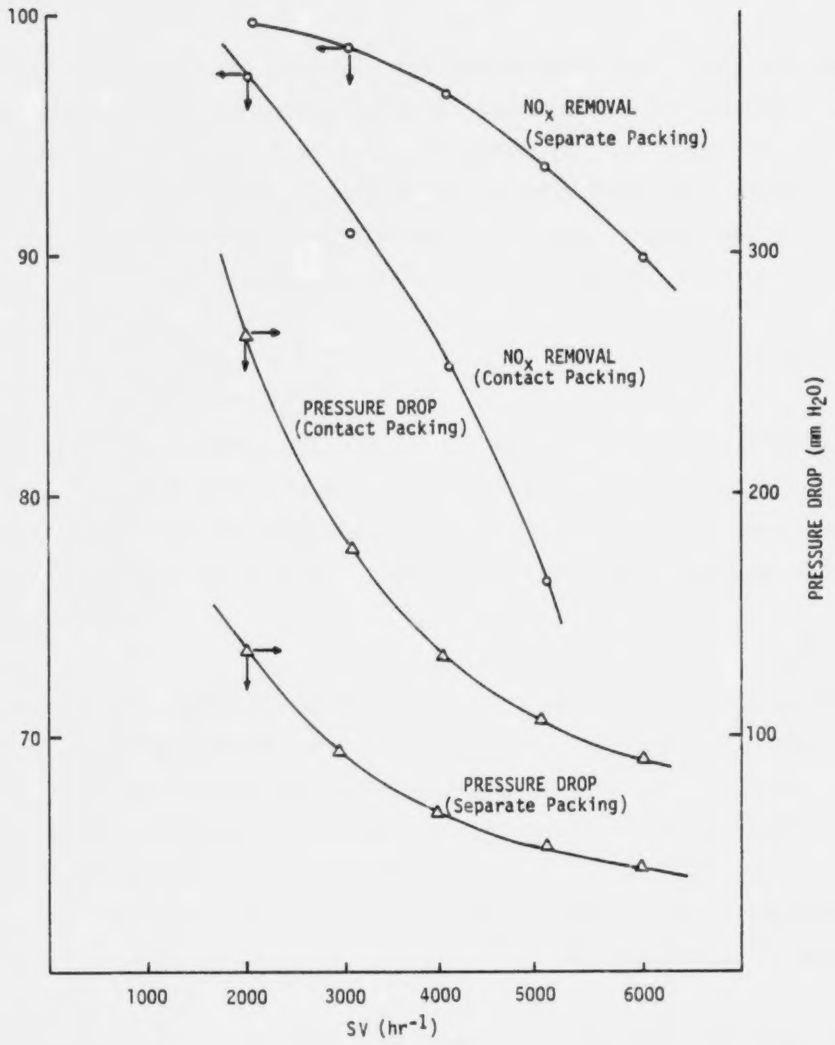


Figure 4-44. Effect of catalyst packing method on NO_x removal and pressure drop (fixed gas velocity, varying catalyst volume).[7]

flow inside and outside the tubes is equal to the ratio of the inside and outside surface areas. The diamond and square packings (see Figure 4-43, B) perform comparably at the same gas flow ratios.

The practical best dimensions for the tube were found to be 20 mm outside diameter and 14 mm inner diameter (Figure 4-45). The tube has a wall thickness of 3 mm. By using a tube of this size, 97 percent of the NO_x was removed at 350°C with an NH_3/NO_x mole ratio of 1.0. Ammonia leakage was below 5 ppm (Figure 4-46). A thinner wall reduces the catalyst weight but makes the tube too weak for the 1000 mm length.

4.5.5 Economics

The Ukishima Petrochemical plant cost 260 million yen ($1.3 million) in 1975. Table 4-13 shows Mitsui Engineering's 1977 estimate of plant cost and annualized cost, including 7 years depreciation for 5 different capacities ranging from 13 to 330 MW and 3 different configurations, A, B and C.

Configuration A is similar to that of the Ukishima Petrochemical plant and the cost includes that for a SCR reactor, ammonia storage, ammonia injection and mixing devices, and equipment for measurement and control. In addition, Configuration B includes a fan. Configuration C is for existing boilers and is similar to that of the Mitsui Petrochemical plant and furthermore includes a heater and a heat exchanger. The table also shows the space requirement for each plant.

The cost for B is 10-30 percent more than that for A while that for C is very high. For example, the plant cost for a 330 MW boiler (1,000,000 Nm^3/hr) is 3270, 4360, and 7910 yen/kW ($16.35, $21.80 and $39.55/kW) for A, B, and C, respectively: the annualized cost is 1300, 1770, and 3480 yen/kl ($6.50, $8.85 and $17.40/kl) oil or 0.30, 0.41, and 0.81 yen/kWhr ($0.0015, $0.0020, and $0.0040/kWhr) for A, B, and C, respectively. The

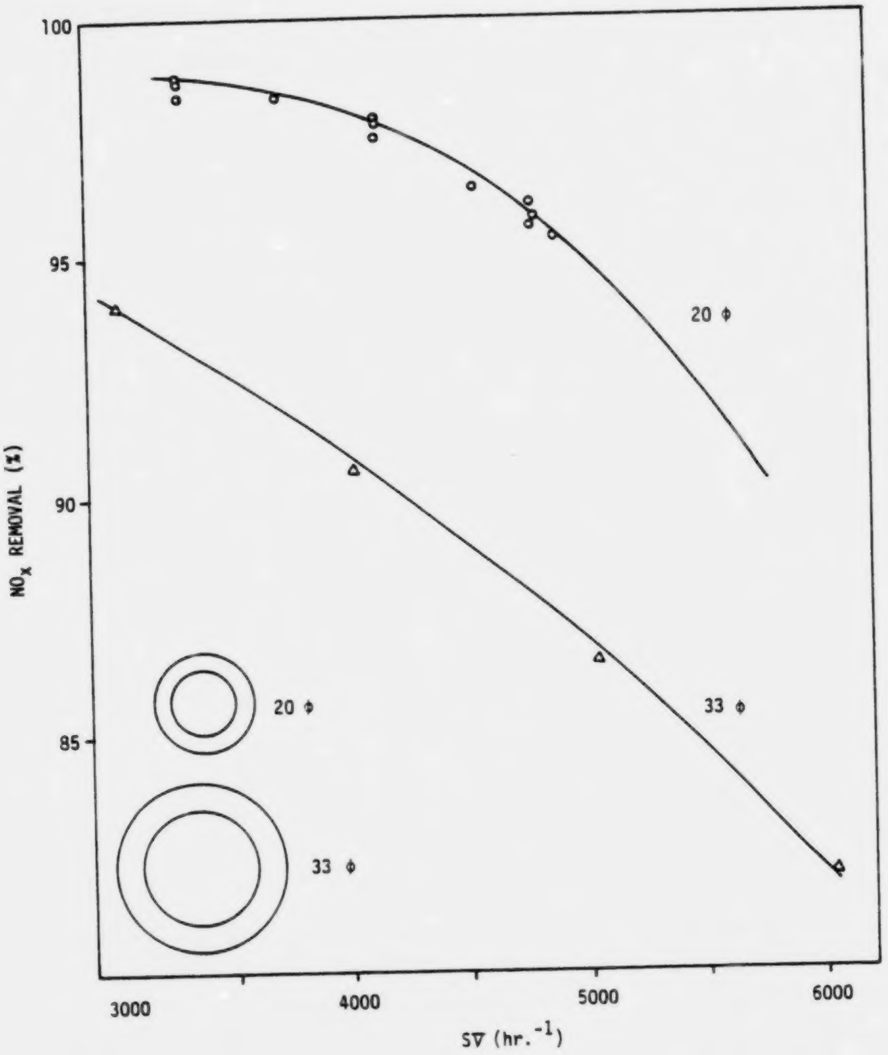


Figure 4-45. SV versus NOx removal for two diameters of tubular catalyst (350°C, separate packing).

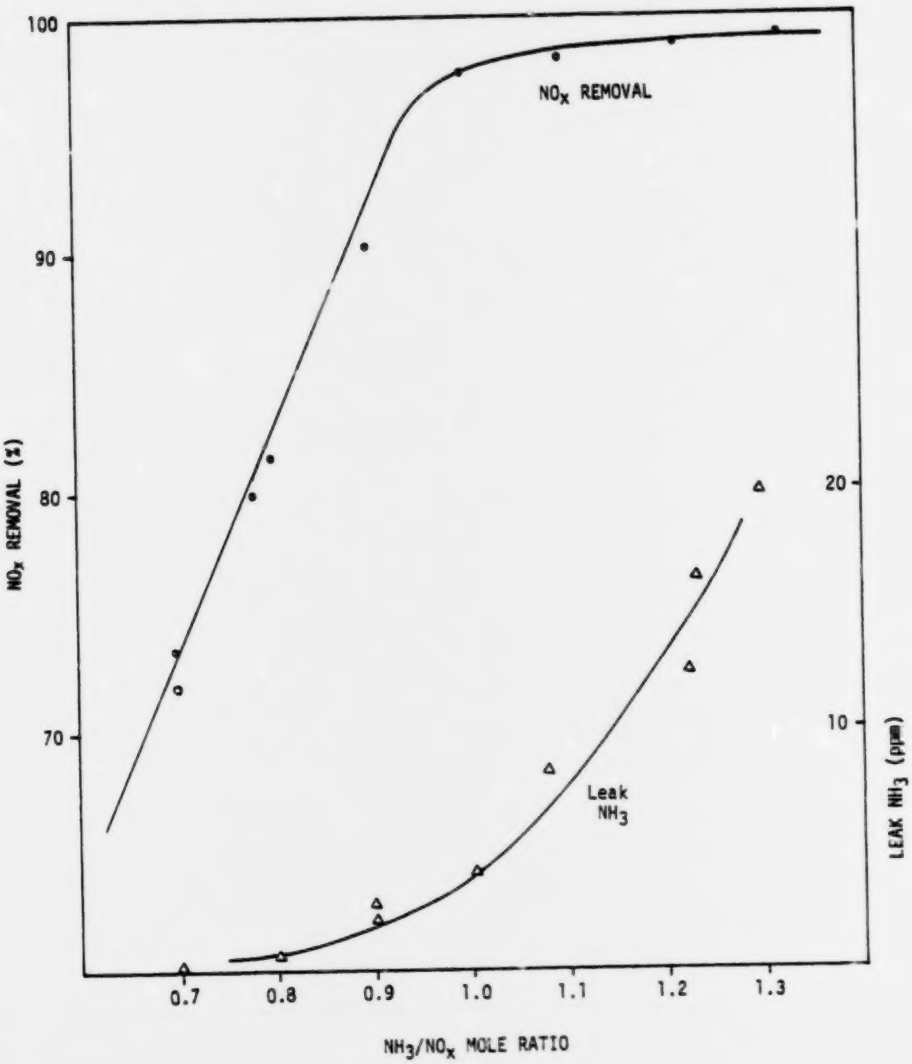
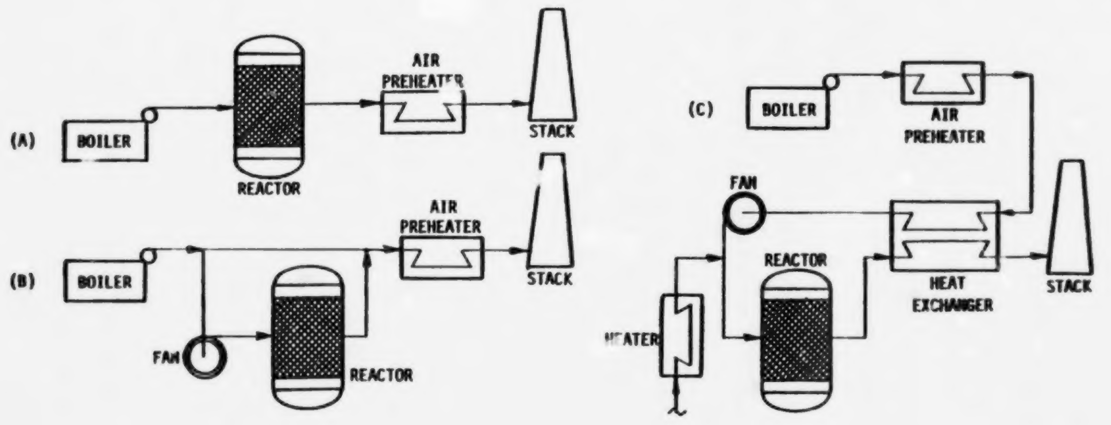


Figure 4-46. Performance of the tubular catalyst with 20 mm diameter (14 mm inner diameter) at 350°C and SV of 4000 hr^{-1}.

TABLE 4-13. ESTIMATED SCR COST OF MITSUI SHIPBUILDING PROCESS WITH TUBULAR CATALYST (1977)

		Investment Cost (10^6 yen, \$5000)			Annualized SCR Cost (yen/kl, \$0.005/kl)			Space Needed (m^2)		
10^3 Nm^3/hr	MW	A	B	C	A	B	C	A	B	C
40	13	153	168	288	2690	3130	5790	140	160	380
100	33	228	264	489	1910	2370	4700	180	240	680
200	66	335	407	792	1620	2080	4140	300	420	970
500	178	596	800	1520	1350	1850	3690	540	740	1900
1000	330	1080	1440	2610	1300	1770	3480	900	1200	3000


(A)
BOILER
REACTOR
AIR PREHEATER
STACK
(B)
BOILER
FAN
REACTOR
AIR PREHEATER
STACK
(C)
BOILER
AIR PREHEATER
FAN
HEATER
REACTOR
HEAT EXCHANGER
STACK

high annualized cost for C is due largely to the fuel requirement for gas heating The space requirement for C is more than triple that for A because of the need for a heat exchanger and heater.

4.5.6 Evaluation

The parallel flow type reactor at the Mitsui Petrochemical Plant (No. 1) was operated smoothly, but has a low space velocity because of the special type of reactor.

The process at the Ukishima Petrochemical plant, which uses a tubular catalyst, has the following advantages: 1) The catalyst has no dust plugging problems when used for flue gas from an oil-fired boiler. 2) Optimum separate packing gives a high NO_x removal efficiency. Although the SV value is not very large, the amount of catalyst required is relatively small. The SV may be much larger when a tube with 20 mm diameter is used. 3) The plant cost is low. 4) The catalyst is based on titanium and may be resistant to gas from a high sulfur fuel.

On the other hand, a high gas velocity in the reactor is needed with the tubular catalyst. This high velocity causes a fairly large pressure drop as in other parallel flow type reactors. The catalyst may also be useful for flue gas from a coal-fired boiler with a full dust load. For particulate-rich gas however, considerable erosion might occur when the superficial gas velocity exceeds 10 m/sec.

The optimum tubular catalyst, 20 and 14 mm in outer and inner diameters, has a thickness of 3 mm. It is desirable to produce a catalyst with a thinner wall which has less weight and yet has a high efficiency and strength. For this purpose, a honeycomb type with a fine structure may be preferred. Tubular catalyst may be suitable for dust-rich gas by which a honeycomb type catalyst with a fine structure may be readily plugged up.

4.6 MITSUBISHI HEAVY INDUSTRIES PROCESS (MHI PROCESS)

4.6.1 Introduction

Mitsubishi Heavy Industries, one of the largest machine producers and plant constructors, has extensively tested SCR catalysts and operated many types of pilot plants for treating various gases, including coal-fired boiler flue gas. For clean gas treatment, MHI constructed two relatively small commercial plants for Osaka Gas and two large ones for Kyushu Electric, one of which went into operation recently (Table 3-1). Those plants use a granular catalyst in a fixed bed. For dirty gas treatment, MHI constructed a plant for Fuji Oil with a honeycomb catalyst and is going to construct a large plant (700 MW) for Chubu Electric. In addition, MHI conducted pilot plant tests with a plate type catalyst. Two large plants with a plate type catalyst began operation recently on utility boilers.

Details of some of the pilot plant tests have been reported. No details of the commercial plants for clean gas from LNG burning have been disclosed, but the clean gas treatment is easy and may not pose any problem. The following sections will describe the Fuji Oil plant which uses a honeycomb catalyst and outline other plants for the treatment of dirty gas.

4.6.2 Chiba (Sodegaura) Plant, Fuji Oil

The SCR plant at the Chiba Refinery, Fugi Oil, can treat 193,000 Nm^3/hr of flue gas from an industrial boiler which burns 0.4 percent sulfur oil containing about 200 ppm SO_2, nearly 120 ppm NO_x, and 15 mg/Nm^3 particulates. The plant, constructed by MHI, uses a honeycomb catalyst. The catalyst unit is cubic and 15 x 15 x 15 cm in size. The catalyst is placed in a duct after the boiler, so that no separate reactor is needed (Figure 4-47).

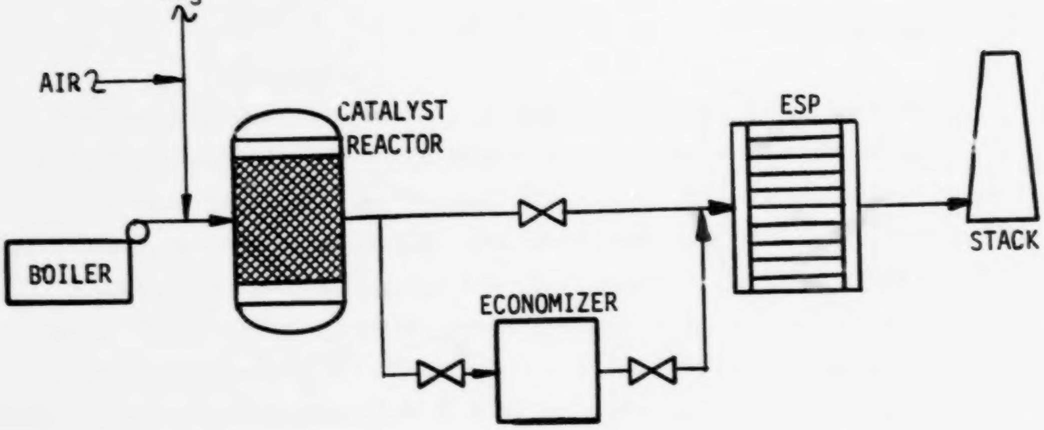


Figure 4-47. Flowsheet of the SCR plant built by MHI at the Chiba Plant, Fuji Oil.

As shown in Figure 4-48, 75 units are packed in package A and 50 units in package B. Thirty-six packages (4 x 9) are placed in a layer and the catalyst bed consists of 3 layers of packages A and a layer of packages B. Thus, there are 9900 units in total with a total bed depth of 1.65 m.

The gas at 350-400°C is passed through the catalyst bed at a superficial velocity of about 9 m/sec and an SV of 6400 hr^{-1}. Pressure drop of the gas through the bed is 120 mmH_2O at full load and 50 mm at 65 percent load. By using 0.75-0.8 mole of NH_3 for each mole of NO_x, 75-80 percent of the NO_x is removed with leak NH_3 (NH_3 in the reactor effluent) less than 1 ppm. At 0.9 mole of NH_3, the removal efficiency reaches 90 percent but the NH_3 in the reactor effluent increases to 2-3 ppm. The plant is normally operated at the low NH_3 ratio of 0.75-0.8 to depress the NH_3 emission. This prevents an ammonium bisulfate deposit in the heat recovery system. (The

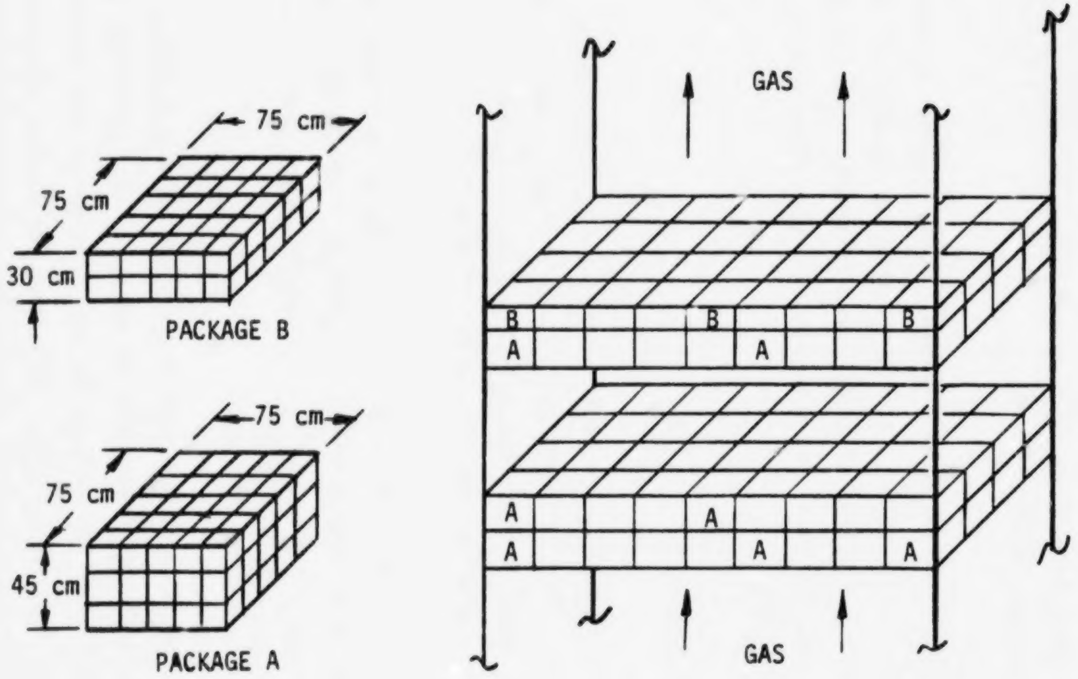

75 cm
75 cm
30 cm
PACKAGE B
75 cm
75 cm
45 cm
PACKAGE A
GAS
B
A
B
A
B
A
A
A
A
A
GAS

Figure 4-48. Packing of honeycomb catalyst at the Chiba Plant, Fuji Oil.

plant has an economizer for heat recovery replacing the usual air preheater.)

The plant was commissioned in January 1978, was run for about a month until the boiler was shut down, then resumed operation in March and has since been operated trouble-free.

The catalyst life is estimated at 2 years. Since neither a separate reactor nor a separate fan is needed, the plant cost is mainly for the catalyst. The very low NH_3 emission which gives virtually no ammonium bisulfate problem as well as the low investment and operation costs, are the advantages of the process.

4.6.3 Parallel Plate Catalyst

MHI has extensively tested a parallel plate catalyst at 5 pilot plants as shown in Figure 4-49. The catalyst plates are produced from either ceramic (castable) or metallic material. The metallic catalyst has a thickness of about 1 mm, and the ceramic one about 8 mm.

The metallic plate catalyst is made by the following two ways: 1) a special alloy plate is chemically treated to dissolve some of the components and make the plate porous and reactive, or 2) powdered catalyst is cemented onto the surface of a metal plate.

The catalyst made by the first method can have a high reactivity but is apt to be poisoned by a high concentration of SO_x. The poisoning is due to the formation of metal sulfates which may plug the pores and reduce the reactive surface ares. Selection of the alloy and the method of chemical treatment are important. By the second method, poisoning can be prevented by using a catalyst known to be SO_x-resistant. A possible problem is removal of the catalyst powder from the metal plate due to the difference in thermal

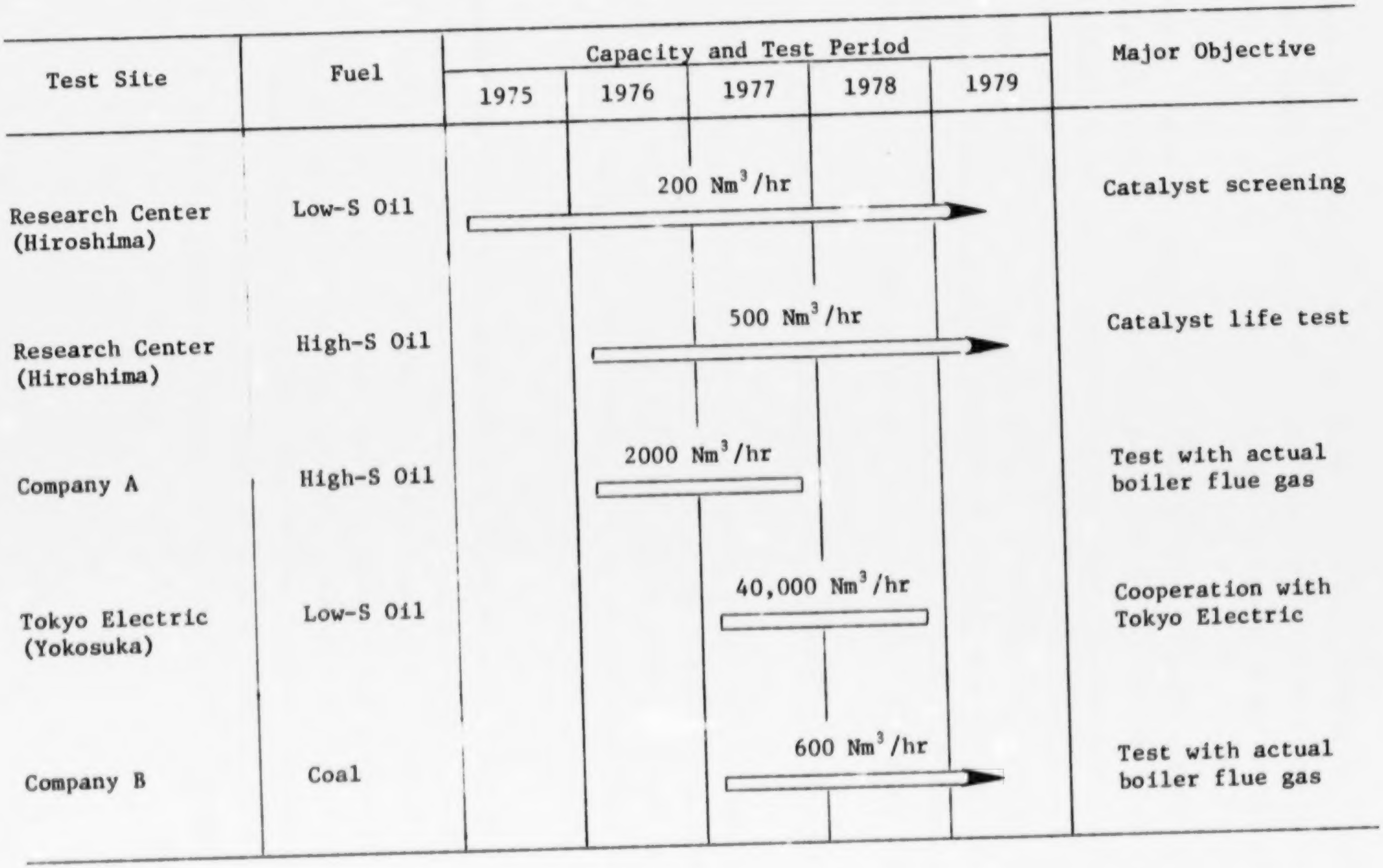


Figure 4-49. MHI's tests with parallel plate catalyst at 5 pilot plants.

expansion coefficients between the metal and the catalyst and also due to the possible corrosion of the metal surface by SO_x. Use of proper materials and a proper method of cementing are important.

The ceramic plate is made by casting the catalyst material. Activity and SO_x resistance of the ceramic plate are similar to those of granular catalysts. A problem with this catalyst is that it must be of a certain thickness to maintain adequate strength; this thickness results in a small surface area per unit volume of catalyst (Table 3-5). Based on screening tests and life tests at MHI's Hiroshima Research Center, plate catalysts with suitable qualities have been produced and used at three pilot plants with flue gases from high-sulfur and low-sulfur oils and coal (Figure 4-49).

4.6.4 Cooperative Tests with Tokyo Electric Using Plate Catalyst

Cooperative tests with Tokyo Electric Power have been carried out since March 1977 at Yokosuka Power Station. Plate catalysts were used for 40,000 Nm^3/hr of flue gas from a boiler burning 0.2 percent sulfur oil. A flowsheet of the pilot plant is shown in Figure 4-50. The major equipment installations are shown in Table 4-14.

During the tests, the catalyst plates were placed in a duct between the boiler economizer and the air preheater, particularly on existing boilers. In one test, ceramic catalyst plates, 1 m x 1 m with 10 mm thickness, were installed with 14 mm clearance. About 90 percent NO_x removal was attained with 1 mole NH_3 for each mole of NO_x at 300-380°C. Gas velocity was 7-8 m/sec and SV about 1000 hr^{-1}. Ammonia leakage was kept below 20 ppm and the ammonium bisulfate problem in the air preheater was not serious. There has been neither dust clogging nor catalyst poisoning.

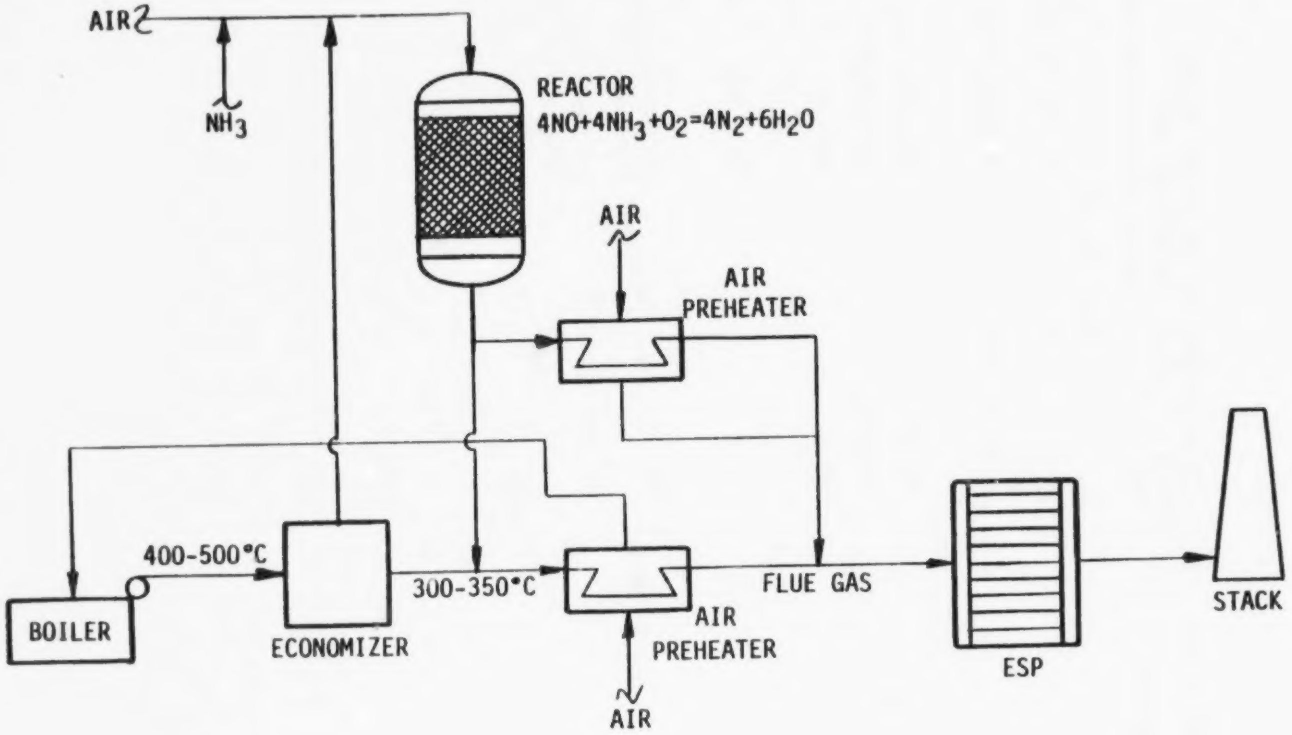

AIR
NH3
REACTOR
4NO+4NH3+O2=4N2+6H2O
AIR
AIR PREHEATER
400-500°C
300-350°C
BOILER
ECONOMIZER
AIR PREHEATER
AIR
FLUE GAS
ESP
STACK

Figure 4-50. Flowsheet of the pilot plant at Yokosuka Station, with plate catalyst.

TABLE 4-14. MAJOR INSTALLATIONS OF THE PILOT PLANT AT YOKOSUKA STATION, TOKYO ELECTRIC

Equipment	Description	
Reactor	Catalyst Bed	3 x 2 x 8 m
Induced Fan	Capacity	2000 Nm^3/min
	Pressure	500 mmH_2O
	Power	250 kW
Air Preheater	Type	Rotating
Gas Analyzer	NO_x	Chemical Luminescence (2)
	NO_x and SO_x	Ultraviolet Absorption (1)
	NH_3	Chemical Luminescence
		Ion Electrode
Computer	Type	MELCOM 350-7

4.6.5 Large Plants for Utility Boilers

Large SCR plants constructed by MHI for treating flue gas from utility boilers were shown in Table 1-14. Full-scale plants for two new 600 MW LNG-fired boilers began operation in 1978.

Two full-scale SCR plants, 350 MW (1,012,000 Nm^3/hr) and 156 MW (490,000 Nm^3/hr), were constructed by MHI and also began operating in 1978. The plants use a plate catalyst for the flue gas from oil-fired boilers. The catalyst plates are placed in a duct between the boiler economizer and air preheater to remove about 40 percent of the NO_x. The pressure drop is small and is covered by the existing fan. The plants aim at NO_x removal at a minimum cost. No details of the operations have been disclosed yet.

MHI has obtained an order from Chubu Electric Co. for the construction of a full-scale SCR plant for the Chita No. 4 boiler (700 MW oil-fired boiler burning 0.2 percent-sulfur oil) to reduce NO_x from 100 ppm to 20 ppm with ammonia leakage of about 10 ppm. The plant will be completed by February 1980. The existing fan for the boiler has an excess capacity of 100 mmH_2O. It is likely that a honeycomb catalyst will be used to give a pressure drop of less than 100 mmH_2O so that no additional fan would be needed. The investment cost is estimated at 2.1-2.8 billion yen ($10.5 million-$14 million) or 3000-4000 yen/kW ($15-20/kW).

4.6.6 Evaluation

MHI has extensively studied NO_x removal not only by SCR but also by noncatalytic reduction (Section 5.4) and wet processes including simultaneous removal with SO_x (Section 7.2), in attempts to establish reliable, economical processes. The use of a honeycomb catalyst at the Chiba plant, Fuji Oil, appears quite successful: a honeycomb will probably be used for the 700 MW oil-fired boiler of Chubu Electric. The low investment cost of the plant (3000-4000 yen/kW) is due to its simplicity--just adding a reactor without increasing the fan capacity.

The plate catalyst aims at further simplification of the process. A certain thickness, however, is needed for the ceramic plate for maintaining enough strength; therefore a much larger catalyst weight and bed volume is required than for the honeycomb. Metal based thin plates may be preferred for commercial use. The plate catalysts may be best suited for plants which require a moderate NO_x removal ratio of 60-80 percent or which treat the gas after selective noncatalytic reduction to reduce NH_3 and to increase NO_x removal efficiency.

4.7 IHI PROCESS

4.7.1 Introduction

Ishikawajima-Harima Heavy Industries (IHI), one of the largest constructors of boilers and ships, has tested SCR systems treating flue gases from boilers burning gas, oil, and coal at many pilot plants; it has constructed and will construct several large plants with honeycomb catalysts mainly for oil-fired utility boilers. Large-scale tests with a combined system of SNR and SCR have also been carried out. Catalysts by a few producers, including Catalyst and Chemicals Inc. and Sakai Chemical, have been used.

4.7.2 Pilot Plant Tests at Power Stations

Extensive pilot plant tests have been performed jointly with Chubu Electric Power at the Shinnagoya Power Station. There are 2 moving bed reactors with capacities of 6400 and 1000 Nm^3/hr and a reactor with a honeycomb catalyst (800 Nm^3/hr). Also at Taketoyo Power Station is a larger pilot plant (20,000 Nm^3/hr) with a honeycomb catalyst.

Figures 4-51 - 4-54 show test results, NO_x removal versus temperature, SV, NH_3/NO_x ratio, and boiler load for the intermittent moving bed type reactor at Shinnagoya Power Station. The flue gas was from a low-sulfur-oil fired boiler. About 95 percent NO_x removal efficiency was obtained with NH_3 leakage below 10 ppm at 350°C. An NH_3/NO_x mole ratio of 1.0 and an SV of 8000 hr^{-1} were used (Figure 4-53). Figure 4-54 indicates that the NO_x removal efficiency increased at lower load despite the temperature drop because of the decrease in SV. The catalyst was not affected by ammonium bisulfate even at 270°C at the lowest load because of the low SO_x concentration of the gas.

Figures 4-55 and 4-56 show the results of tests with a honeycomb catalyst at Taketoyo Power Station. The flue gas resulted from combustion of crude or heavy oil and contained 150-200 ppm of SO_x. Ninety percent NO_x removal with less than 10 ppm of NH_3 leakage was obtained at 360°C with an SV of 6000 hr^{-1} and NH_3/NO_x mole ratio of 1.0. The pressure drop was only about 40 mmH_2O and did not increase appreciably during 8000 hours of continuous testing. The NO_x removal efficiency also did not change appreciably during the period.

IHI has been operating 3 pilot plants, each with the ability to treat 1000 Nm^3/hr of flue gas from a coal-fired boiler at Isogo Power Station, EPDC. Honeycomb catalysts have been used in two of the plants for flue gas with full particulate load and also for flue gas after fly ash removal by a hot electrostatic precipitator. The tests have been carried out jointly with EPDC and the results have not been disclosed yet. Supposedly there is no erosion of the catalyst except the inlet edge by fly ash at full dust load when the superficial gas velocity is kept below about 5 m/sec (actual gas velocity through the honeycomb below 8 m/sec).

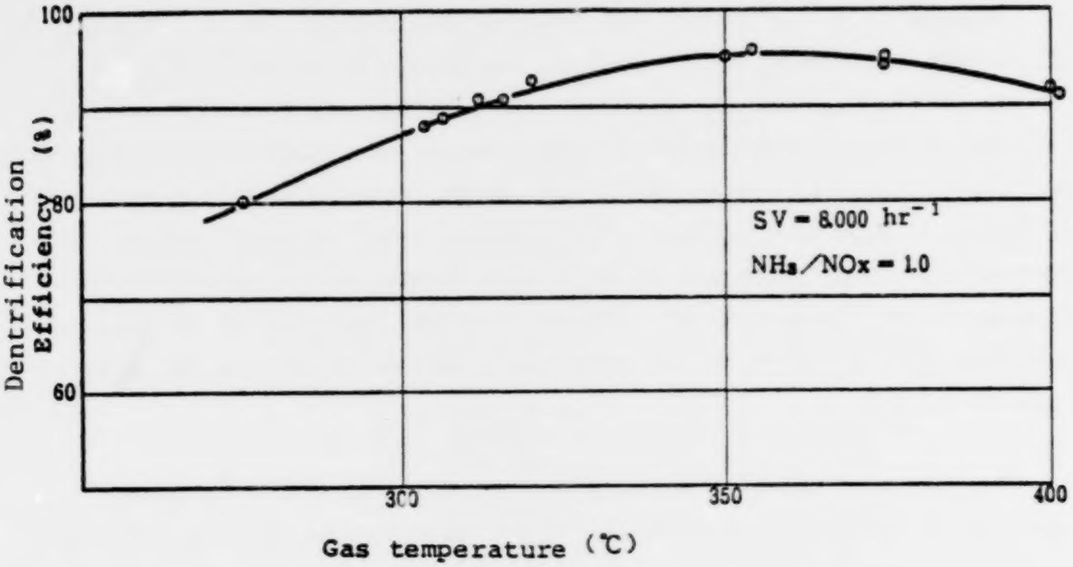


Figure 4-51. Gas temperature versus denitrification efficiency for the moving bed reactor at Shinnagoya Power Station.

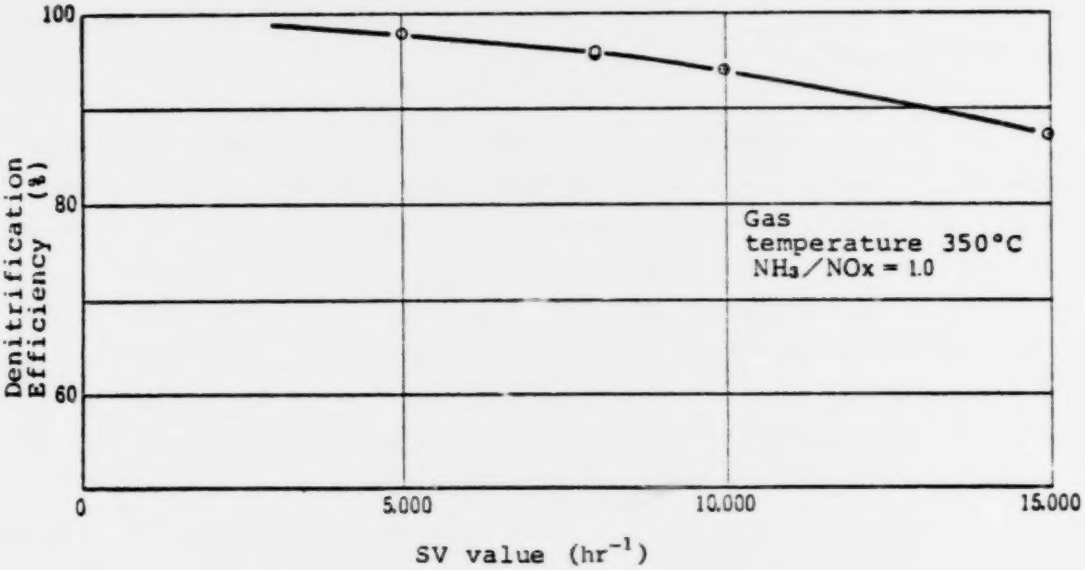


Figure 4-52. SV value versus denitrification efficiency for the moving bed reactor at Shinnagoya Power Station.

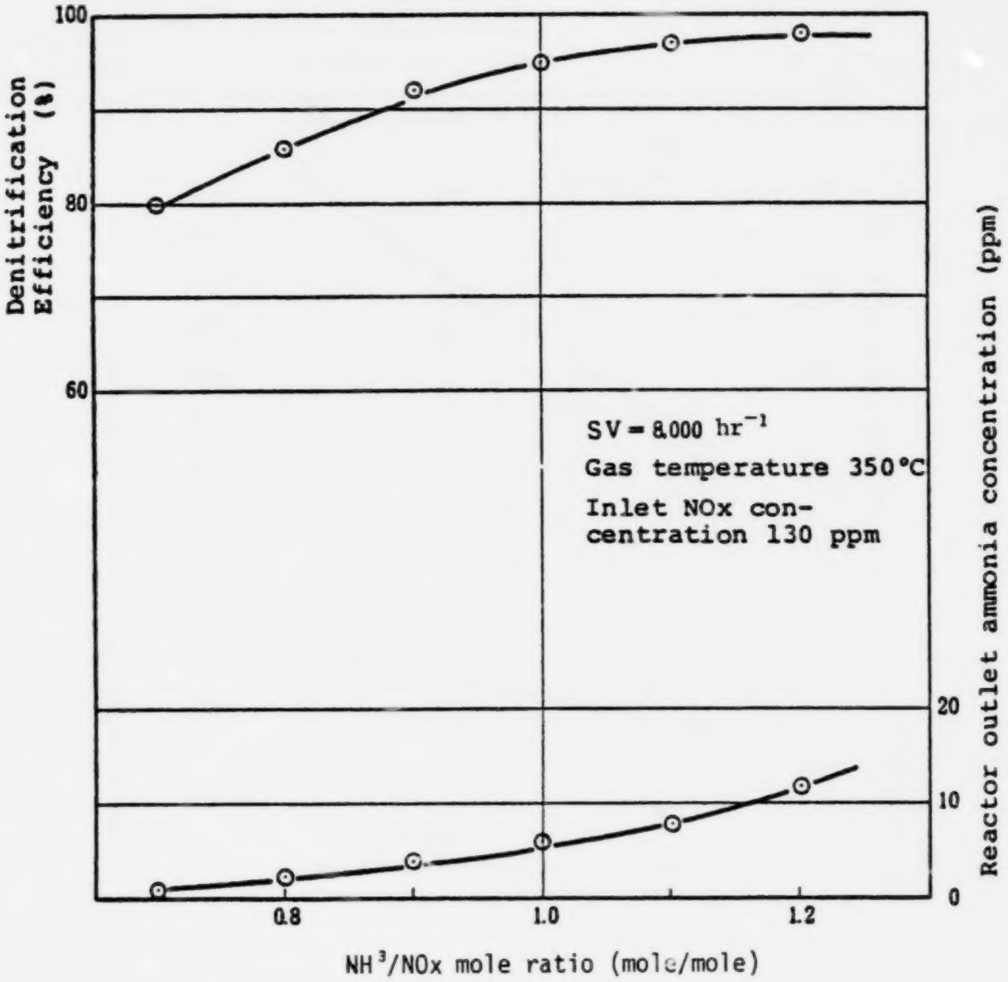


Figure 4-53. NH_3/NO_x mole ratio versus denitrification efficiency and reactor outlet ammonia concentration for the intermittent moving bed reactor at Shinnagoya Power Station.

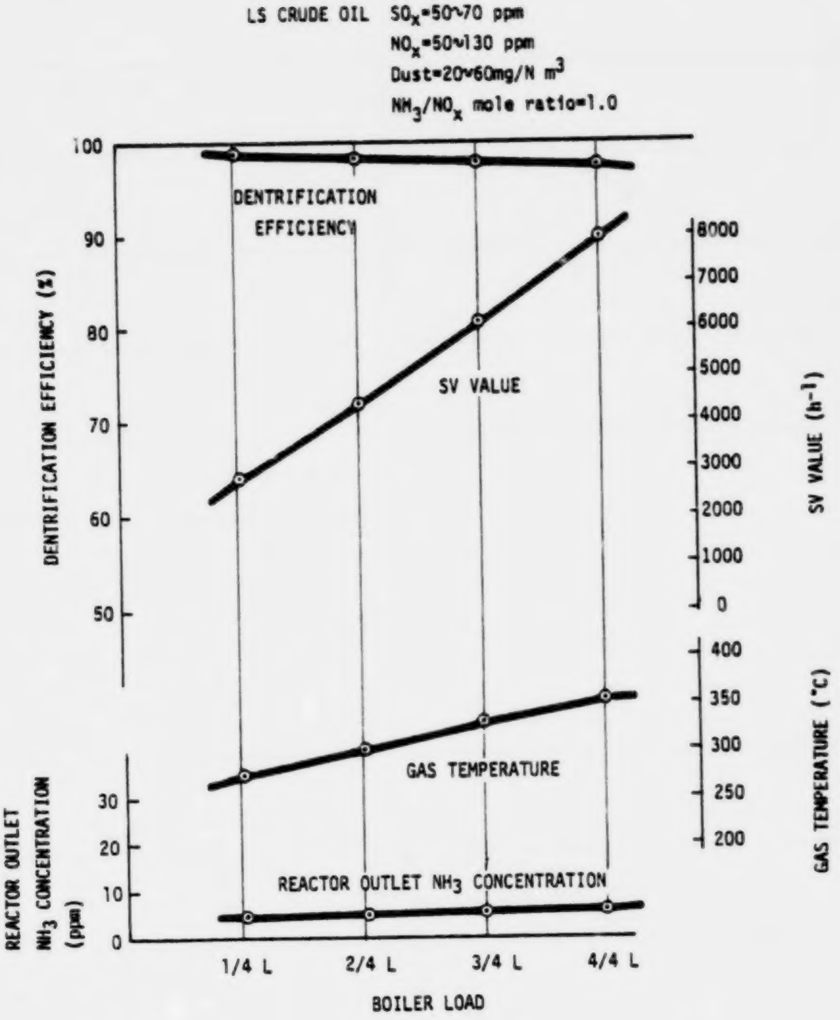


Figure 4-54. Relation between boiler load and denitrification efficiency for the intermittent moving bed reactor at Shinnagoya Power Station.

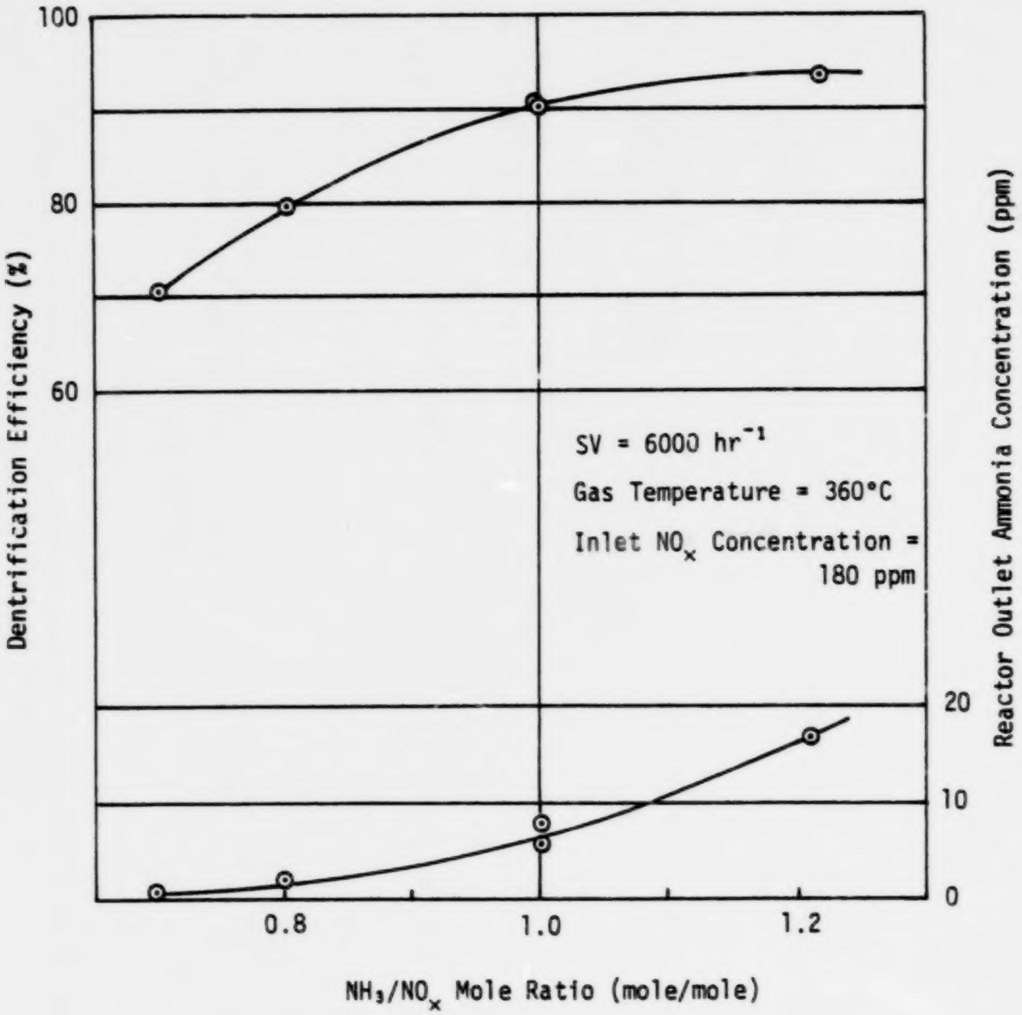


Figure 4-55. NH$_3$/NO$_x$ mole ratio versus denitrification efficiency versus reactor outlet ammonia concentration for the honeycomb catalyst at Taketoyo Power Station.

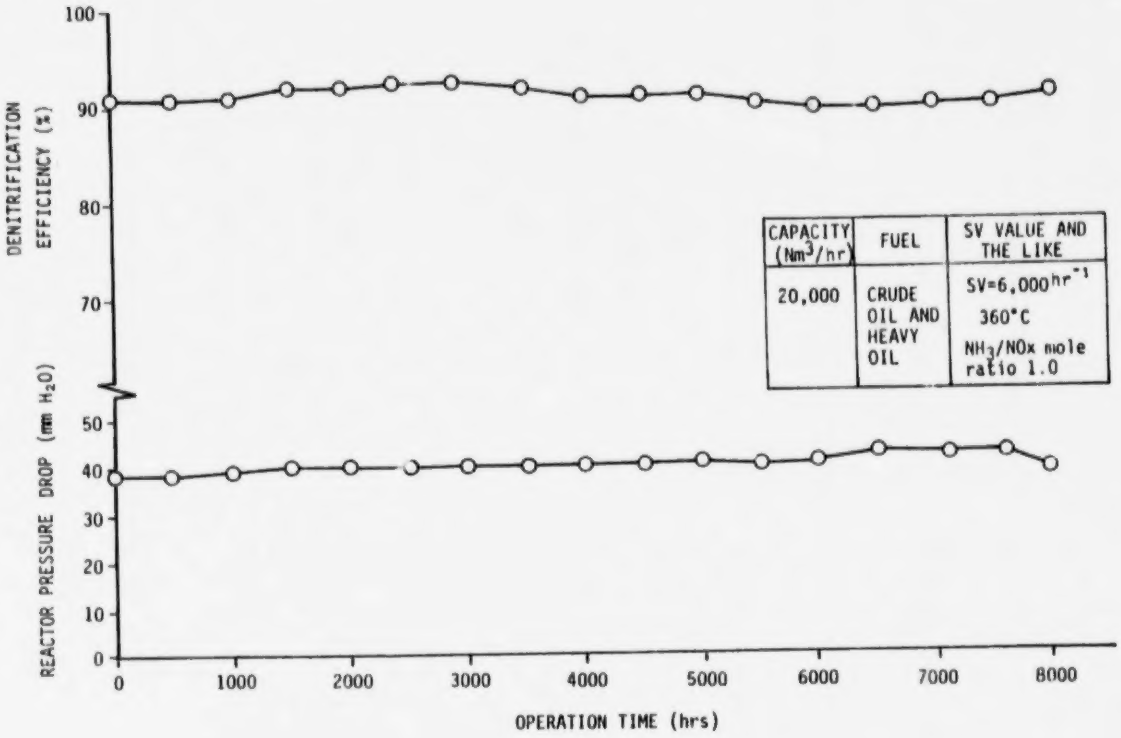


Figure 4-56. Catalyst life test results for the honeycomb catalyst at Taketoyo Power Station.

4.7.3 Large-Scale Plants

Table 4-15 lists large-scale test plants and commercial plants constructed by IHI.

TABLE 4-15. LARGE-SCALE SCR PLANTS BY IHI

User	Plant Site	Reactor Type	Gas Treated (Nm^3/hr)	Completion
Ajinomoto	Kawasaki	Moving Bed	200,000	January 1978
Company A	--	Fixed Bed*	1,020,000	April 1978
Company B	--	Fixed Bed*	453,000	June 1978
Chugoku Electric	Kudamatsu	Fixed Bed	1,000,000	April 1979
Chugoku Electric	Kudamatsu	Fixed Bed	1.900.000	July 1979
Tohoku	Niigata	Fixed Bed	1.660.000	August 1981

* Combination with selective noncatalytic reduction.

The Ajinomoto plant uses a granular catalyst in a moving bed to treat flue gas from an industrial boiler which burns grade C heavy oil. The other 5 plants are for power companies and use a honeycomb catalyst in a fixed bed to treat flue gas from utility boilers which burn low-sulfur oil. All of the plants treat flue gas from a boiler economizer at 350-400°C as shown in Figures 4-57 and 4-58.

The plants for companies A and B are for existing boilers and use the combined SNR and SCR system to remove 50-60 percent of NO_x. Ammonia is injected into the boiler at 850-1000°C to remove 25-30 percent of NO_x. A small amount of catalyst is placed in the duct between the boiler economizer and the air preheater for further reduction of NO_x and for reduction of

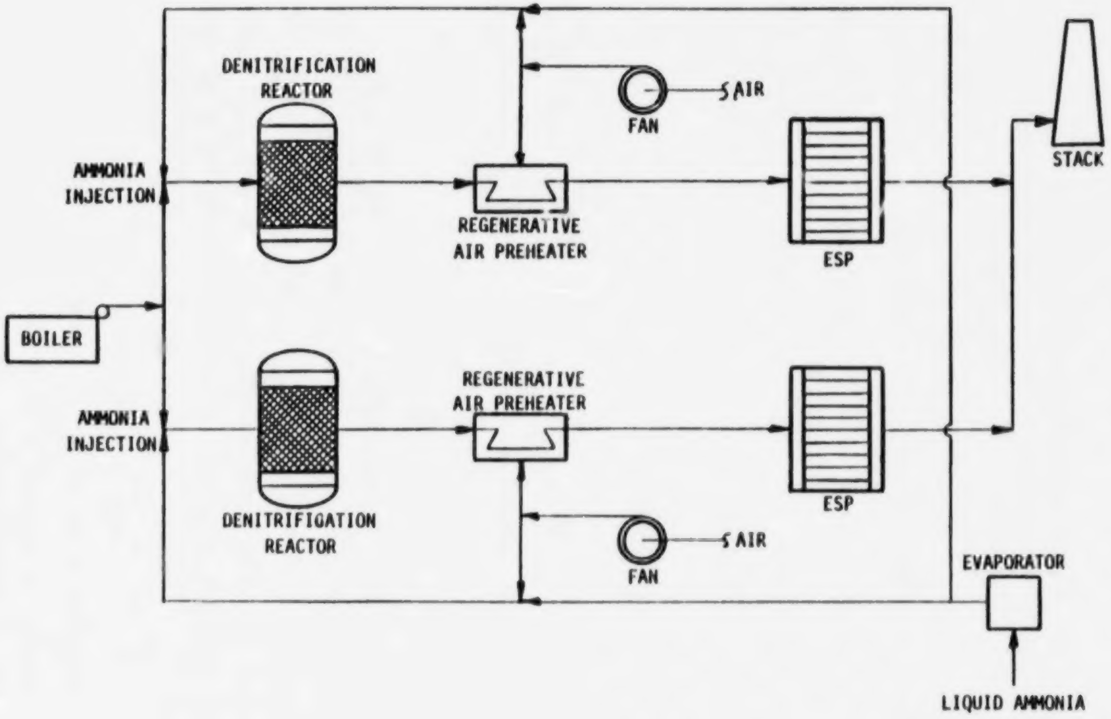
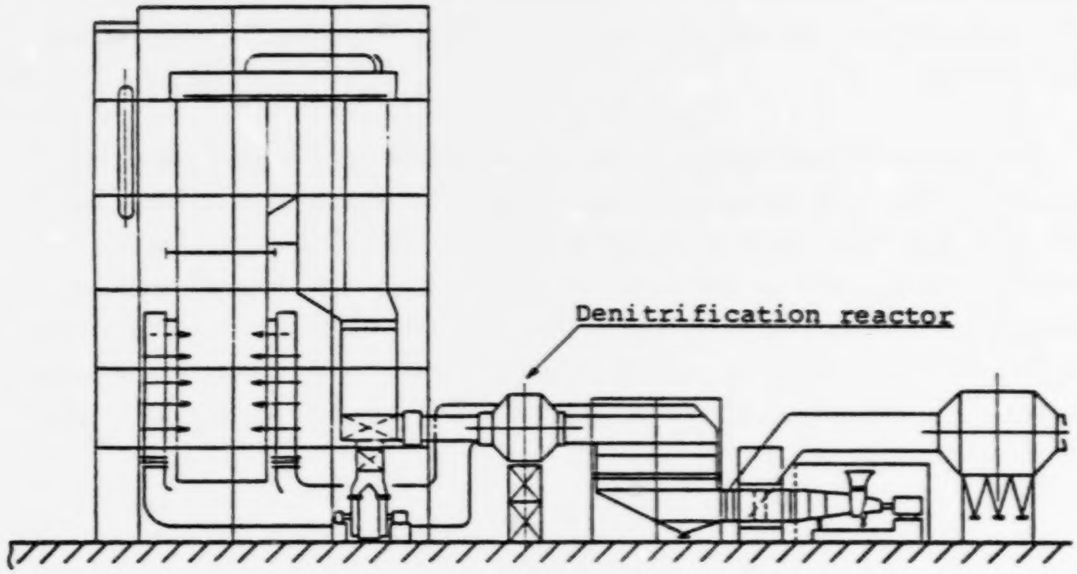
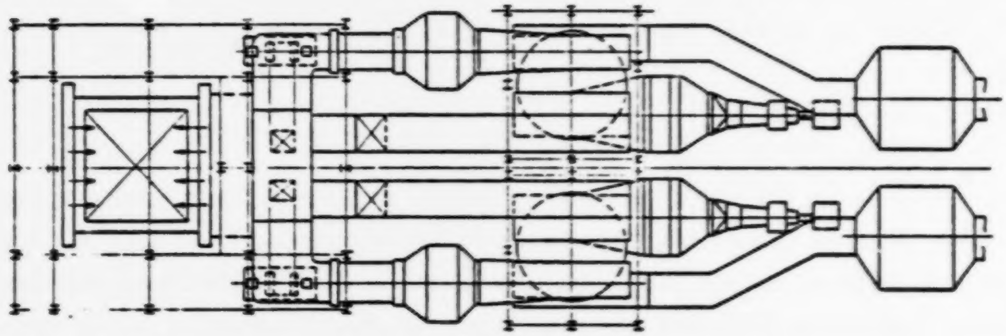

DENITRIFICATION REACTOR
AMMONIA INJECTION
REGENERATIVE AIR PREHEATER
FAN
AIR
ESP
STACK
BOILER
AMMONIA INJECTION
REGENERATIVE AIR PREHEATER
ESP
DENITRIFIGATION REACTOR
FAN
AIR
EVAPORATOR
LIQUID AMMONIA

Figure 4-57. Standard flowsheet for the boiler denitrification equipment at 5 large IHI plants for combustion gas from heavy oil.


Denitrification reactor

Side View



Plan

Figure 4-58. Plant equipment layout (example) of 5 large IHI plants.

ammonia leakage to about 10 ppm. Although details of the plants have been kept confidential, the system aims at NO_x reduction without increasing the fan capacity.

The plant for company C is under construction. It should remove 80 percent of NO_x. The Kudamatsu plant, Chugoku Electric, is also under construction and should also remove 80 percent of the NO_x from the total 2,900,000 Nm^3/hr of flue gas from two boilers which burn naphtha and low-sulfur oil. The structure of the reactor for the Kudamatsu Plant is similar to that shown in Figure 3-26. The Niigata Plant, Tohoku Electric, is being designed for 60 percent NO_x reduction. NH_3 leakage will be kept at 10 ppm or below at those plants.

4.7.4 Economics

No economic data have been disclosed. However, it is said by a catalyst dealer that the cost of a 150 x 150 x 500 mm honeycomb catalyst is about equal to that of granular catalyst for a unit volume, although it is higher for a unit weight.

4.7.5 Evaluation

The honeycomb catalyst used by IHI is efficient. It removes 90 percent of NO_x with 10 ppm of NH_3 leakage at an SV of 6000 hr^{-1} and with a pressure drop of only 40 mmH_2O. And, the honeycomb catalyst costs about the same as other catalysts for dirty gas for a unit volume. Therefore, for a dust-rich gas, the honeycomb catalyst can be advantageous over the granular catalyst, which requires a moving bed. The honeycomb catalyst seems resistant to SO_x and free from dust clogging. Such desirable features of the catalyst and proper design of the reactor may have led IHI to construct the large SCR plants for flue gas from utility boilers.

The test plants for companies A and B remove 50-60 percent of NO_x by a combined system of SNR and SCR, while the commercial plant to be constructed at Niigata for Tohoku Electric is designed to remove 60 percent of NO_x with SCR only. Use of only SCR may be preferred if there is enough space to install a reactor or to enlarge a portion of the duct so that a catalyst can be inserted. With SCR only, ammonia consumption is much less, process control is easier, a higher removal efficiency is attainable when needed, and the investment cost including the catalyst may not be much different from the cost of the combined system.

4.8 KURABO PROCESS (KNORKA PROCESS)

4.8.1 Introduction

Kurabo is one of the largest textile companies with an engineering division. It has constructed many FGD plants with sodium and ammonia scrubbing. Kurabo has pioneered the development of the SCR process for dirty flue gas without precleaning from oil-fired boiler economizers at 350-400°C. In 1974, it completed a 5000 Nm^3/hr pilot plant with a moving bed reactor packed with an alumina-based catalyst and a thermal regeneration system for the catalyst. A larger pilot plant (30,000 Nm^3/hr) has been operated since 1975.

In 1976, Kurabo made tests with a particulate-rich gas prepared by adding coal fly ash to oil-fired boiler flue gas. Recently, Kurabo developed an SO_x-resistant catalyst based on titanium oxide which does not require thermal regeneration. Tests to minimize the ammonia in the reactor effluent have been carried out by using a microcomputer system.

Kurabo has licensed the process to TRW, Inc. of the United States.

4.8.2 Process Description

A flowsheet of the Kurabo process is shown in Figure 4-59. The reactor for the 30,000 Nm^3/hr pilot plant has three elements capable of treating 10,000 Nm^3/hr each (Figure 4-60). In each element a spherical catalyst on an alumina support (carrier), 5 mm in diameter, moves slowly and continuously downward. The gas passes through the elements in a cross flow. Since the thickness of the element, or the catalyst layer, is fairly small and the gas velocity through the catalyst is relatively low, the pressure drop in the reactor is kept below 100 mmH_2O.

An SV of 7000-10,000 is normally used. The flue gas contains about 1600 ppm SO_2, 280 ppm NO_x, and nearly 100 mg/Nm^3 particulates. More than 90 percent of the NO_x and about 80 percent of the particulates are removed in the reactor at 350-400°C with an NH_3/NO_x mole ratio of about 1.0. An example of the operating data is shown below:

NO_x concentration (ppm)	280 (inlet)	18 (outlet)
Dust content (mg/Nm^3)	94 (inlet)	17 (outlet)
Gas volume (Nm^3/hr)	24,000	
SV (hr^{-1})	8,000	
SO_2 concentration (ppm)	1,650	
Gas temperature (°C)	400	
Pressure drop in reactor (mmH_2O)	65	
Ammonia consumption (liters/min.)	106.5	

The catalyst discharged from the reactor is screened to remove particulates, heated to 800°C to decompose aluminum sulfate and to reactivate the catalyst, and is then returned to the reactor. One cycle requires about 100 hours, therefore only a small portion of the catalyst is regenerated at one time. The catalyst has a high strength of more than 10 kg per granule; loss by crushing is less than 5 percent of the total catalyst used yearly. After more than 10,000 hours' operation the catalyst activity

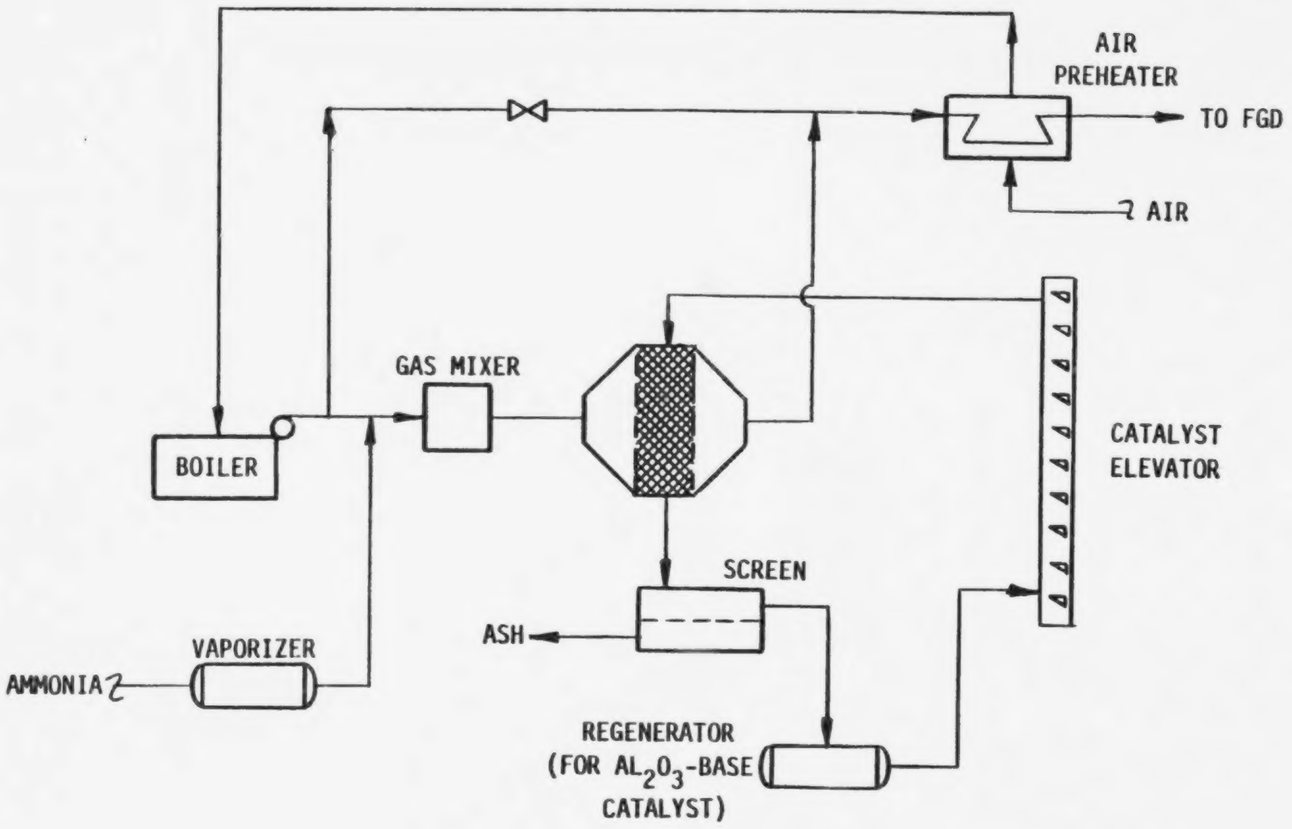

AIR PREHEATER
TO FGD
AIR
GAS MIXER
BOILER
CATALYST ELEVATOR
SCREEN
ASH
VAPORIZER
AMMONIA
REGENERATOR (FOR AL_2O_3-BASE CATALYST)

Figure 4-59. Flowsheet of the Kurabo (Knorka) SCR process.

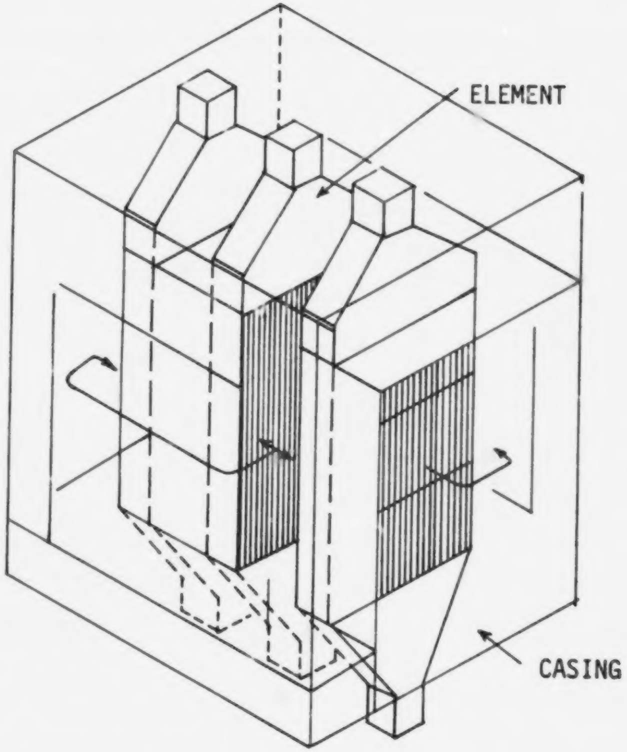

ELEMENT
CASING

Figure 4-60. Structure of the Kurabo moving bed reactor.

has shown a slight decrease; catalyst life is estimated at over 16,000 hours.

The relationship of the NH_3/NO_x mole ratio to the NO_x removal efficiency and ammonia leakage (ammonia concentration of the gas discharged from the reactor) is shown in Figure 4-61.

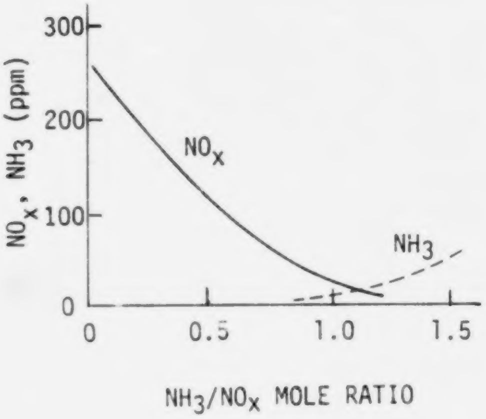


Figure 4-61. Relationship of NH_3/NO_x mole ratio to outlet NO_x, NH_3 concentrations in the Kurabo moving bed reactor.

Tests have also been carried out with a TiO_2-based catalyst that is resistant to SO_x, and requires no thermal regeneration. Reactivity is adequate at 350°C and life is estimated at 2 years. Use of the TiO_2 catalyst may be more economical than that of Al_2O_3-based catalysts.

4.8.3 Economics

The investment and annualized costs for SCR, as estimated by Kurabo for the TiO_2-based catalyst, are shown in Tables 4-16 and 4-17. The investment cost ranges from 4100 to 9300 yen/kW ($20.50 to $46.50/kW) for

TABLE 4-16. PLANT COST IN 1978 (MILLIONS OF YEN, $5000) FOR THE KURABO KNORCA PROCESS

Item	Capacity (Nm^3/hr)		
	30,000	100,000	500,000
Reactor, Heater, Etc.	33	80	252
Ducts and Pipings	16	30	96
Instrumentation	19	28	78
Transportation and Installation	5	12	37
Foundation	7	15	46
Subtotal	82	165	509
Catalyst	10.5	35	175
Total	92.5	200	684

TABLE 4-17. ANNUALIZED SCR COST FOR THE KURABO KNORCA PROCESS*

Item	30,000 Nm^3/hr		100,000 Nm^3/hr		500,000 Nm^3/hr	
	10^6 yen/yr ($5000/yr)	yen/kl oil ($0.005/kl)	10^6 yen/yr ($5000/yr)	yen/kl oil ($0.005/kl)	10^6 yen/yr ($5000/yr)	yen/kl oil ($0.005/kl)
Depreciation	11.89	756	25.71	490	87.94	335
Interest	3.70	235	8.00	153	27.36	104
Ammonia**	6.85	435	22.80	435	57.12	218
Power (12 yen/kWhr)	7.17	455	19.96	380	84.27	322
Catalyst (2.5 x 10^6 yen/m^3)	5.78	367	19.25	367	96.25	367
Steam (2 yen/kg)	--	--	0.19	4	0.95	2
Labor	2.00	127	2.00	38	4.00	15
Maintenance, etc.	1.20	76	2.50	48	7.60	30
Total	38.59	2451	100.41	1915	365.49	1393

* C grade heavy oil (No. 6 heavy oil, 0.78 kl/10,000 Nm^3; NO_x, 280 ppm; 8400 hours annual operation; average yearly load, 80 percent; gas temperature, above 350°C (upstream of air preheater); requires no auxiliary burner; catalyst, TiO_2-support catalyst.

**160 yen/kg ($0.80/kg) in cylinders for small amounts, 80 yen/kg ($0.40/kg) in tanks for large amounts.

30,000-500,000 Nm^3/hr, equivalent to 10-167 MW. The annualized cost ranges from 1390 to 2450 yen/kl ($6.95 to $12.25/kl) oil or from 0.31 to 0.54 yen/kWhr ($0.0016 to $0.0027/kWhr) assuming 8400 hours' operation in a year.

4.8.4 Recent Studies

Kurabo has studied reducing the ammonia in reactor effluent without reducing the NO_x removal efficiency by using microcomputer control. The computer system not only controls the NH_3/NO_x ratio based on the automatic analysis of inlet and outlet NO_x and NH_3 concentrations but also corrects possible temporary errors of the NO_x analyzer due to corrosion by SO_x or other problems. With the control, the NH_3/NO_x mole ratio is always kept at slightly below 1.0 to maintain an NO_x removal efficiency of over 90 percent and an NH_3 leakage of below 10 ppm.

Kurabo has tested the effects of halogens in flue gas on catalysts. The TiO_2-based catalyst was much more stable than the alumina-based catalyst against attack by chlorine and fluorine in the gas.

Kurabo has designed a larger reactor element with a unit capacity of 50,000 Nm^3/hr. About 40 elements will be needed for a 500 MW coal-fired boiler. To treat the coal-fired boiler flue gas, Kurabo intends to use a multicyclone with 80-90 percent particulate removal ahead of the reactor to reduce the fly ash to 2-3 grams/Nm^3. While the amount of fly ash is still sufficient to cause plugging, Kurabo has found a way to pass the ash through the moving bed without causing clogging. Since the ash is not sticky, it is blown off by flue gas at a certain velocity and by the movement of the catalyst granules in the reactor.

4.8.5 Pilot Plant for Coke Oven Flue Gas (Kurabo-Niigata Process)[3]

Kurabo has licensed their process for coke oven flue gas to Niigata Engineering Co., which constructed a pilot plant at the Funamachi Works, Nakayama Steel. This plant can treat 2000 Nm^3/hr of flue gas from a coke oven. The gas composition fluctuates every 20-30 minutes over a wide range--NO_x: 35-400 ppm, SO_x: 80-250 ppm, O_2: 3-15 percent, CO_2: 18.5-20.5 percent, H_2O: 9-11 percent, and below 35 mg/Nm^3 of particulates. The following 6 kinds of catalysts have been tested:

	NKN-1	NKN-2	NKN-3∿6*
Shape	Spherical	Spherical	Various
Size (mm)	4-6	3.5-4.5	4-6
Composition	$Cu-Al_2O_3$	$Cu-Al_2O_3$	Various
Crushing Strength (kg/granule)	8-10	10-15	Various

---

* Including SO_x-resistant and low-temperature catalysts.

The flowsheet of the plant is similar to that of Kurabo's pilot plant (Figure 4-59) except that a gas-gas heat exchanger and a heater are installed to heat the gas from 180°C. Test results with the catalysts NKN-1 and NKN-2 are shown in Figure 4-62. NKN-2 is smaller and gives a higher efficiency but causes a larger pressure drop; the pressure drop in the reactor was 28-35 mmH_2O with NKN-1 at an SV of 10,000 hr^{-1} and 35-45 mmH_2O with NKN-2 at an SV of 7000 hr^{-1}.

Since the gas does not contain much SO_x and particulates, the catalysts were not noticeably affected. For example, use of the catalyst NKN-2 for 1100 hours without moving the bed gave neither an appreciable increase in pressure drop nor a decrease in NO_x removal efficiency. The results of tests with the other catalysts (NKN-3 - NKN-6) have not been disclosed. These catalysts include those based on TiO_2 which are not only SO_x-resistant but are also efficient at a relatively low temperature of 300-350°C.

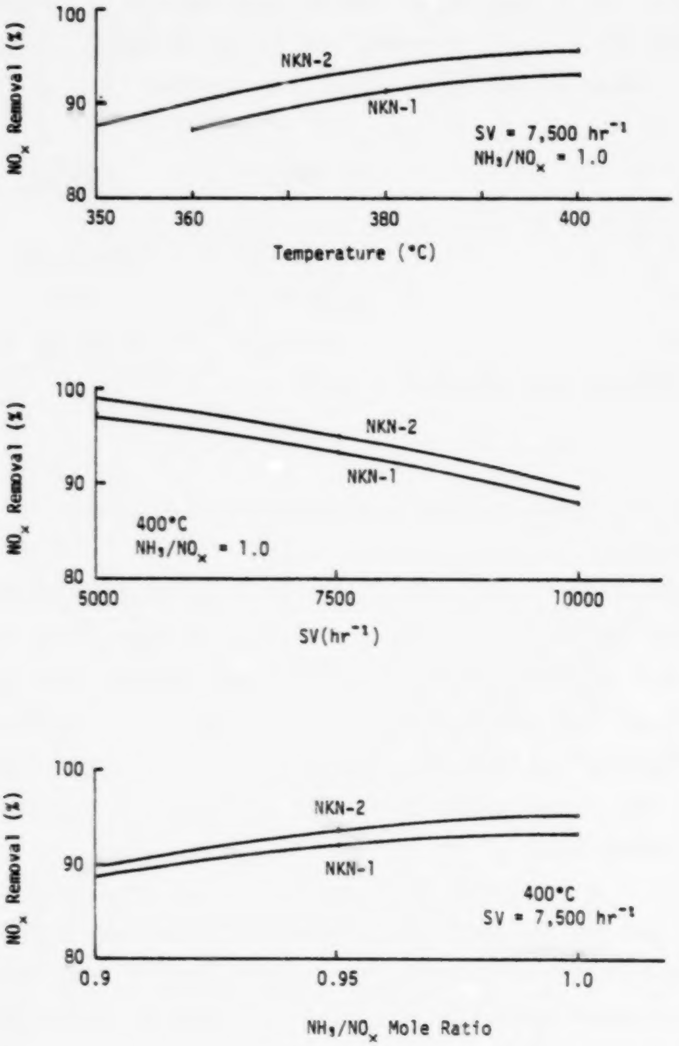


Figure 4-62. Results of the Kurabo-Niigata process at a pilot plant for coke oven flue gas.

4.8.6 Evaluation

Kurabo, as a pioneer in dirty gas treatment with a moving bed reactor, has considerably improved the plant operation and the catalyst. The microcomputer system that reduces ammonia leakage to 1-2 ppm may have a considerable significance. Further development of the system is desired so that it can control a big reactor with many elements, each of which may perform differently.

When the multicyclone is used for coal-fired boiler flue gas, another particulate removal facility is needed after the air preheater. The total cost of the multicyclone and the cold dust removal facility may be less than that of a hot electrostatic precipitator for dust removal before the reactor. Moreover, the considerable amount of fly ash passing through the air preheater will reduce the ammonium bisulfate problem in the preheater (Section 3.5).

The advantage of the Kurabo process is enhanced when the process is used with an ammonia-scrubbing FGD process such as that developed by Kurabo. Most ammonia discharged from the reactor is caught by the scrubber and utilized for SO_2 recovery. In other scrubbing processes ammonia will accumulate in the scrubber liquor and may cause a problem. Even when used with ammonia scrubbing, it may be desirable to lower the level of ammonia in the reactor effluent so that the ammonium bisulfate problem in the air preheater and the plume problem in the scrubber can be minimized.

4.9 KUREHA PROCESS

4.9.1 Introduction

Kureha Chemical Industries is a medium-sized chemical company credited with developing many new petrochemical and electrochemical processes which have been used in many countries. Kureha recently developed a new SCR catalyst reactive at 150°C, the usual temperature of the boiler flue gas after the air preheater. The catalyst is therefore designed for application to existing boilers with which it is difficult to obtain gas at 400°C for SCR with conventional catalysts.

The new catalyst, however, is poisoned by SO_x. SO_x also causes an ammonium bisulfate deposit which lowers the activity of the catalyst. Therefore, flue gas containing SO_x will first have to be treated to reduce the SO_x content to 1 ppm. Sodium scrubbing and a wet electrostatic precipitator are needed for the purification as discussed below. A 5000 Nm^3/hr pilot plant was put into operation in February 1977.

4.9.2 Process Description

Catalysts usually have a carrier such as Al_2O_3 or TiO_2. The Kureha catalyst consists of base metal compounds and does not have such a carrier. The catalyst is a cylinder 5 mm in diameter and 10 mm tall. It costs about 1.5 million yen/ton ($7500/ton), no more than other SCR catalysts. The catalyst is used in a fixed bed, with a superficial gas velocity of 0.75 m/sec and an SV of 5000 hr^{-1}. It removes about 90 percent of NO_x with 1.0-1.1 moles of NH_3 for each mole of NO_x.

To reduce SO_x in flue gas to less than 1 ppm, Kureha's sodium acetate FGD process may be useful but the process has not yet been commercialized. Conventional FGD processes may reduce the SO_x content of the scrubber effluent to about 10 to 200 ppm. Kureha has reduced the SO_x concentration to 1 ppm by sodium scrubbing and a wet electrostatic precipitator, as shown in Figure 4-63.

The purified gas is heated to 120-125°C by a heat exchanger and to 150°C by an indirect steam heater, injected with ammonia, and sent to the reactor.

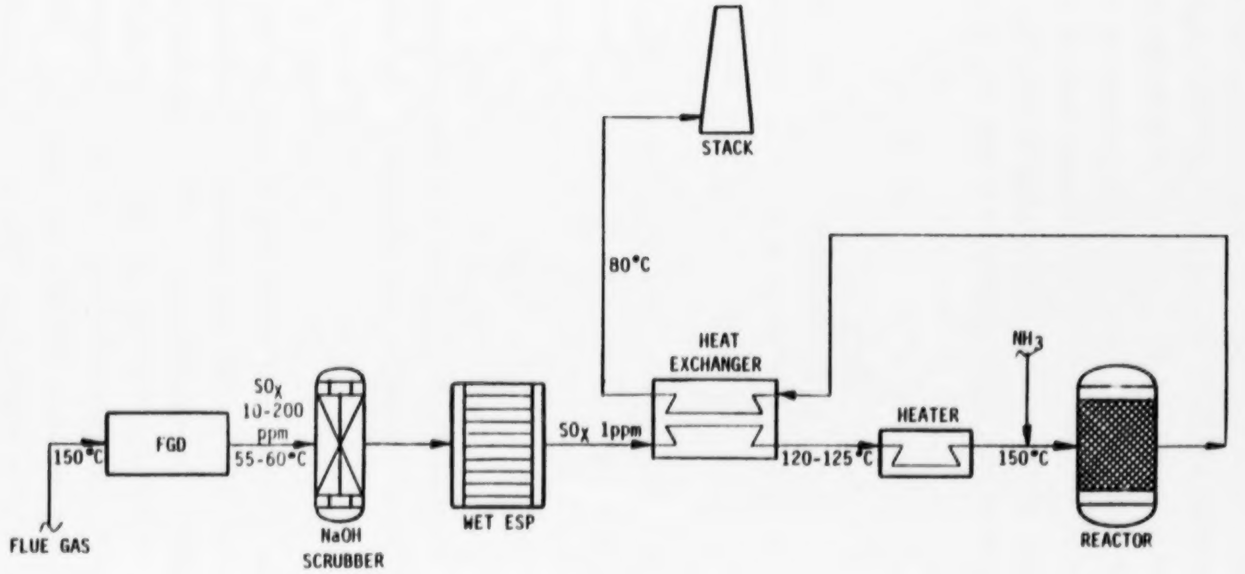

STACK
80°C
HEAT
EXCHANGER
NH$_3$
HEATER
SO_x
10-200
ppm
55-60°C
FGD
150°C
SO_x 1ppm
120-125°C
150°C
FLUE GAS
NaOH
SCRUBBER
WET ESP
REACTOR

Figure 4-63. Flowsheet of Kureha SCR process for treating flue gas discharged from a conventional FGD system.

4.9.3 Economics

Kureha estimates a total investment cost of about 12,000 yen/kW ($60/kW) including sodium scrubbing and a wet electrostatic precipitator. The SCR unit itself costs about 3000 yen/kW ($15/kW). The following raw materials and utilities are required for removal of 99 percent of the SO_x and 90 percent of the NO_x from 100,000 Nm^3/hr of flue gas from an oil-fired boiler, after passing through an FGD system, containing 50 ppm SO_x, 200 ppm NO_x and 100 mg/Nm^3 particulates. A catalyst life of 1 year is assumed.

Raw Material		Utility	
NaOH	24.4 kg/hr	Electricity	293 kW
NH_3	14 kg/hr	Process Water	1.0 tons/hr
Catalyst	22 tons/year	Steam	2.1 tons/hr

The annualized cost, including 7 years' depreciation, is about 0.85 yen/kWhr ($0.0042/kWhr) for dirty gas.

4.9.4 Evaluation

Kureha's catalyst has outstanding activity at low temperatures but its commercial application is limited because it is poisoned by SO_x in dirty flue gas.

Compared with the other FGD-SCR combination system used in the Yokkaichi plant, the Shindaikyowa Petrochemical system (4.2), the Kureha process requires less energy for the gas heating (25-30°C temperature rise as compared with 80-90°C at Yokkaichi) and has no ammonium bisulfate problem in the heat exchanger. On the other hand, the Kureha process requires sodium scrubbing and a wet electrostatic precipitator. These clean the gas but add considerably to the total cost. The by-product sodium sulfite from the FGD process may be a disposal problem where there is no demand for the sulfite.

The Kureha process should be used with a highly efficient FGD process such as the Kureha sodium acetate process. A wet electrostatic precipitator is needed even with an efficient FGD process because a small portion of SO_3 is not caught by FGD.

If a catalyst is found which is SO_x-resistant, reactive at 150°C, and does not require gas purification, the Kureha process can be more widely used. In this case, ammonium bisulfate will deposit on the catalyst to lower its activity but the bisulfite can be removed by occasionally heating the gas to 350°C as is done by JGC (4.4.6).

Because it can be applied without any pretreatment, Kureha's catalyst is useful for cooled clean flue gas such as that from existing boilers which burn natural gas. For the gas leaving the economizer of a new natural gas-burning boiler, SCR with other catalysts at 300-400°C might be preferred because a much larger SV, up to 20,000 hr^{-1}, could be used.

4.10 KOBE STEEL PROCESS

4.10.1 Introduction

Kobe Steel, one of the largest steelmakers and plant constructors in Japan, has tested SCR with moving beds at two pilot plants (1000 Nm^3/hr each). They also constructed a prototype plant for Kansai Netsukagaku (Table 3-1). Kobe also has operated a SCR pilot plant with a honeycomb catalyst (10,000 Nm^3/hr).

Details of the prototype plant have not been disclosed. The operation data of the pilot plants will be described below.

4.10.2 Pilot Plant Test with Moving Bed[3]

Since early 1976 Kobe Steel has operated two pilot plants with catalyst in a moving bed. Each can treat 1000 Nm^3/hr of flue gas. One is on a coke oven at the Amagasaki Iron Works and the other is on an iron-ore sintering machine at the Kakogawa Works. Since the flue gases are discharged at 150-200°C, they are heated to 250-400°C by a heat exchanger and a heater.

A flowsheet of the Kakogawa plant is shown in Figure 4-64. Two catalysts, a vanadium catalyst 8-10 mm in diameter and an iron catalyst 4-6 mm in diameter, have been used at the plant. Their initial activities are shown in Figures 4-65 and 4-66. The results of 1000 hours' operation of the pilot plant with the vanadium catalyst are shown in Figures 4-67 and 4-68. The flue gas contains 160-195 ppm NO_x, 160-350 ppm SO_x, and 20-40 mg/Nm^3 particulates. Over 90 percent of the NO_x was removed at 350°C with an NH_3/NO_x mole ratio of 1.2 and an SV of 10,000 hr^{-1}. The catalyst bed is 20 cm thick. The pressure drop in the reactor was normally between 40 and 60 mmH_2O and increased to above 100 mmH_2O late in the test period. The pressure drop was lowered to 50 mmH_2O by increasing the catalyst moving rate.

4.10.3 Pilot Plant Test with Honeycomb Catalyst

Since September 1975, Kobe Steel has occasionally operated a pilot plant which can treat 10,000 Nm^3/hr of flue gas from a boiler burning coke oven gas, blast furnace gas, and a low sulfur oil. The flue gas contains 30-50 ppm NO_x and 150-180 ppm SO_x with 20-30 mg/Nm^3 particulates. The gas leaving the boiler economizer at 320-370°C is injected with ammonia and introduced into a reactor with a honeycomb catalyst in a fixed bed. The density of the honeycomb is about 0.5 ton/m^3; about 0.7 m^3 of the catalyst is placed in the reactor. The gas volume fluctuates between 7000 and 14,000 Nm^3/hr so that the SV ranges between 10,000 and 20,000 hr^{-1}. The NO_x in the gas is reduced to 5 ppm at NH_3/NO_x mole ratio of 1.2 and a 1.5-3 m/sec

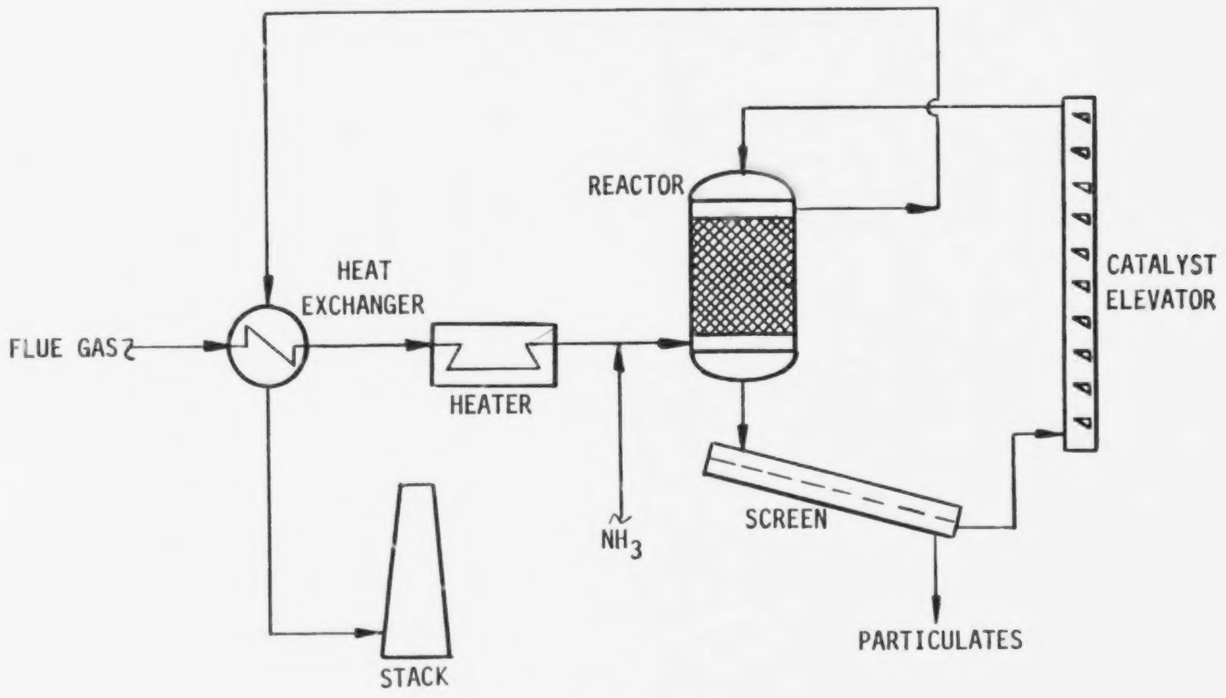

FLUE GAS
HEAT
EXCHANGER
HEATER
STACK
NH_3
REACTOR
SCREEN
PARTICULATES
CATALYST
ELEVATOR

Figure 4-64. Flowsheet of pilot plant at Kakogawa Works, Kobe Steel.

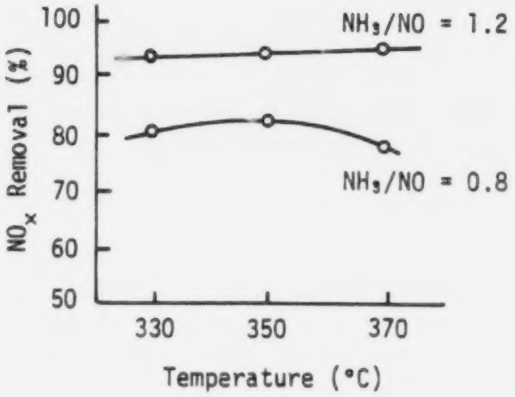


Figure 4-65. Initial activity of Kobe Steel's vanadium catalyst (SV = 10,000 hr^{-1}).

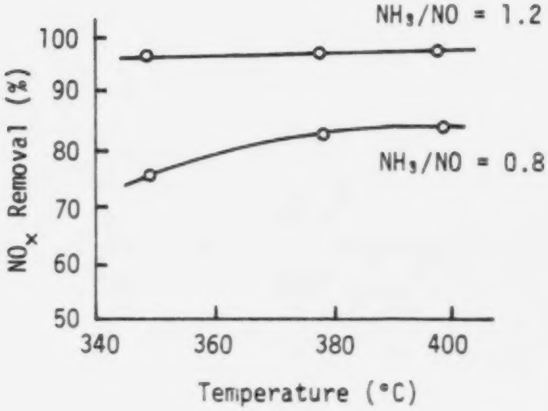


Figure 4-66. Initial activity of Kobe Steel's iron catalyst (SV = 5000 hr^{-1}).

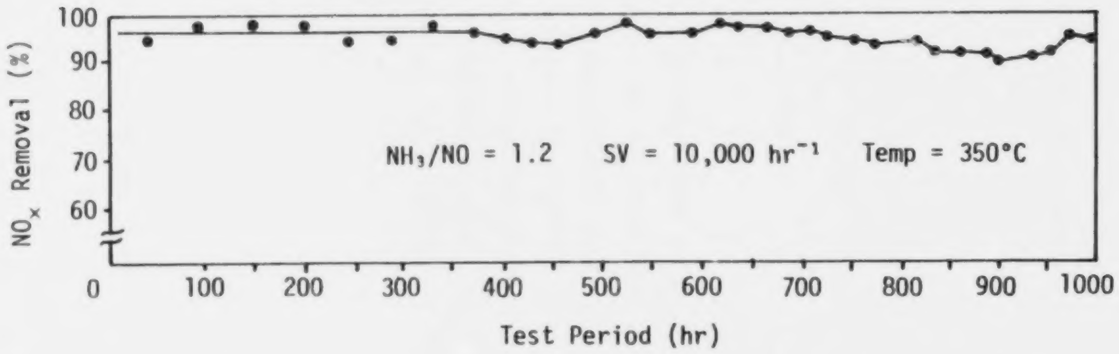


Figure 4-67. NO_x removal efficiency for the first 1000 hours of operation at the Kakogawa pilot plant with vanadium catalyst in a moving bed.

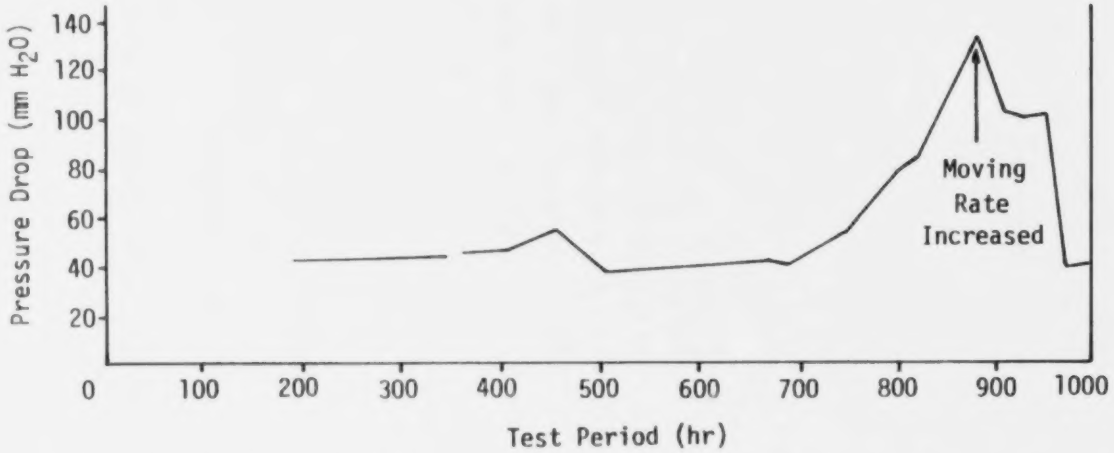


Figure 4-68. Change of pressure drop for the first 1000 hours of operation at the Kakogawa pilot plant with vanadium catalyst in a moving bed.

gas velocity through the catalyst (actual velocity). The pressure drop in the reactor ranges from 30 to 50 mmH_2O.

The catalyst is SO_x-resistant. The reactor has a soot blower to eliminate dust deposited on the catalyst. The plant has been operated trouble-free with occasional soot blowing. Seventy-five kW of power are required for the flue-gas fan. The SCR unit cost 70 million yen in 1975.

Kobe Steel recently succeeded in producing a ceramic honeycomb catalyst with a thin wall (0.5 mm) and has conducted pilot plant tests.

4.10.4 Evaluation

The moving bed reactor and the catalyst appear to have been working well, but they have not been in operation long enough for precise evaluation. The honeycomb catalyst appears promising because of the high efficiency and a small pressure drop. Particularly, the thin wall honeycomb has a very large surface area per catalyst weight ratio and should be highly effective. Further tests are desired to determine the applicability of the honeycomb to larger plants and the catalyst life in gases richer in SO_x and dust.

4.11 OTHER SCR PROCESSES

4.11.1 Mitsui Toatsu Process

Mitsui Toatsu Chemical, one of the largest chemical companies in Japan, has developed two types of granular SCR catalysts, MTC-102 and MTC-104. The MTC-102 catalysts are for clean gas with less than 5 ppm SO_x and are reactive at low temperatures as shown in Figures 4-69 and 4-70. The MTC-104 catalysts are resistant to SO_x (Figures 4-71 and 4-72) and are highly capable of ammonia decomposition. Virtually no NH_3 is detected in the reactor outlet when the NH_3/NO_x mole ratio is kept below 1.2. To treat

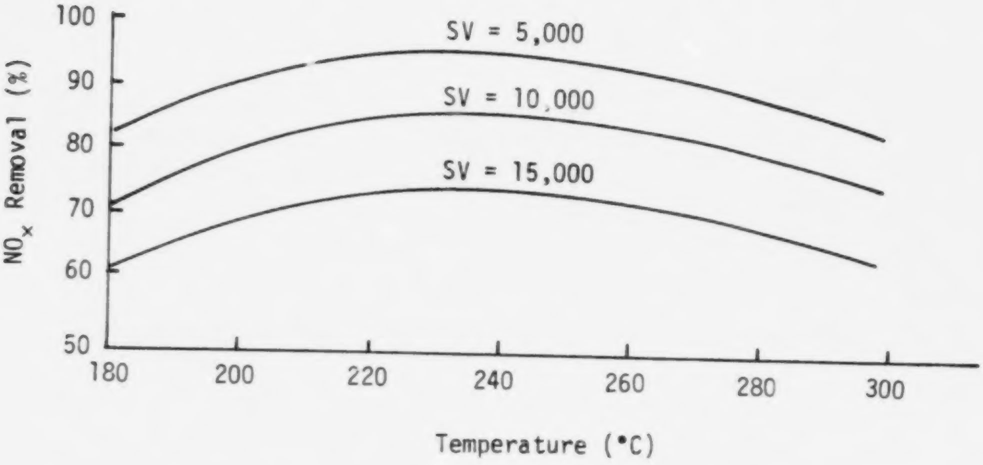


Figure 4-69. Performance of catalyst MTC-102 on a flue gas from LPG burning.

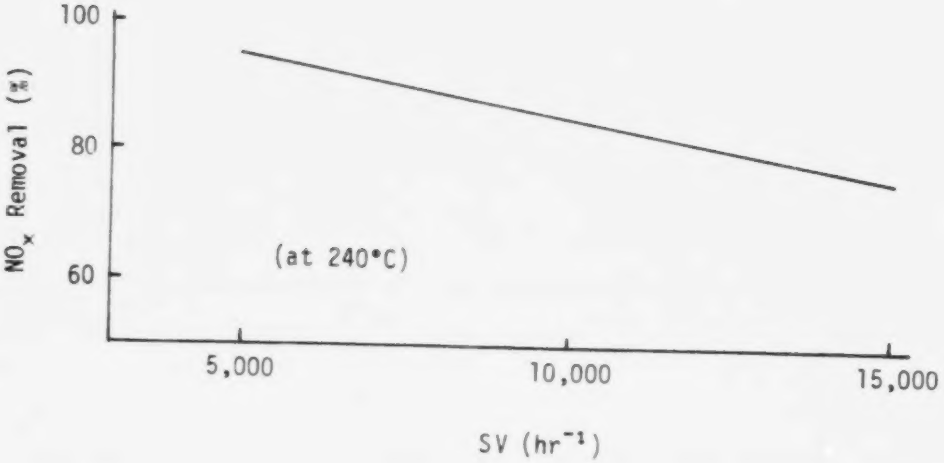


Figure 4-70. SV versus NO$_x$ removal for the catalyst MTC-102 on a flue gas from LPG burning.

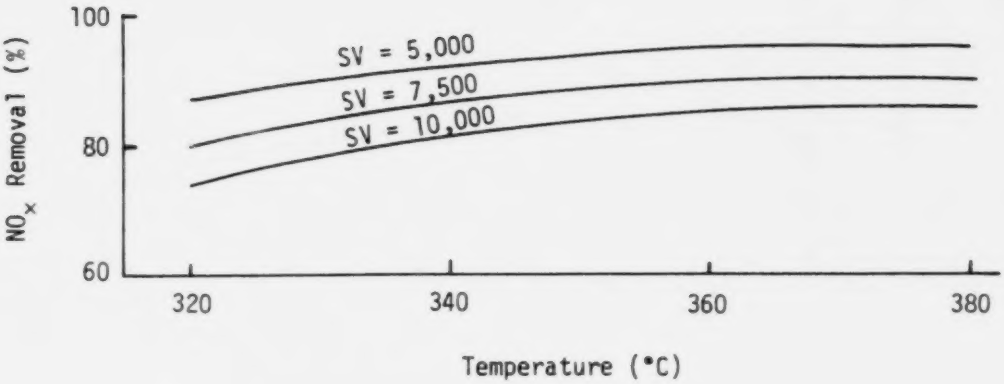


Figure 4-71. Performance of catalyst MTC-104 on the flue gas from heavy oil burning.

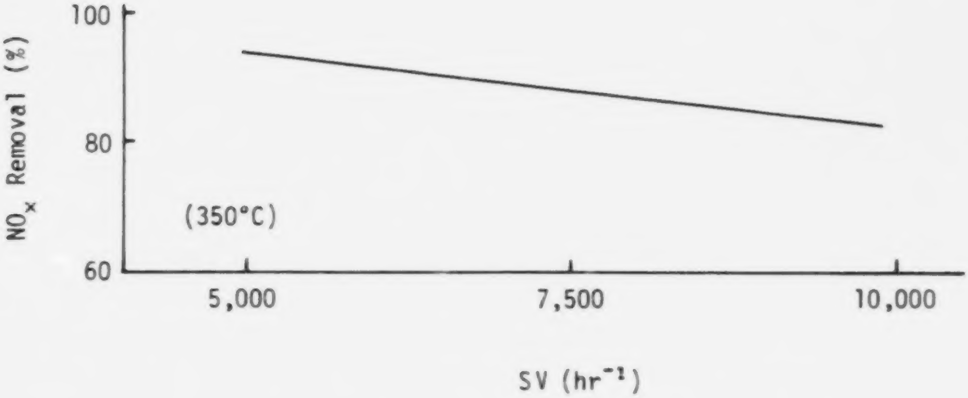


Figure 4-72. SV versus NO$_x$ removal for catalyst MTC-104 on the flue gas from heavy oil burning.

flue gas from heavy oil burning, Mitsui Toatsu has developed a simple particulate removal facility in which a granular catalyst is used in a fixed bed.

Seven recently constructed commercial plants for clean gas use the Mitsui catalysts. (Five of the larger ones are shown in Table 3-2). All seven have been operated without trouble. Mitsui Toatsu Chemical made the basic design of the plants; detailed design and construction were by Toyo Engineering, a related company, or by Ishikawajima-Harima Heavy Industries. Mitsui Toatsu Chemical has obtained an order from the USSR to construct an SCR plant for the treatment of 100,000 Nm^3/hr of flue gas from a fertilizer plant which uses nitric acid to decompose phosphate ore.

Investment and annualized costs are listed in Table 4-18. Investment cost is fairly high, but plant operation is quite reliable and requires minimal labor.

4.11.2 Sumitomo Heavy Industries SCR Process

Sumitomo Heavy Industries (SHI) has constructed and operated a prototype FGD plant with activated carbon in a moving bed, and also constructed a pilot plant in 1976 at the Kokura Works, Sumitomo Metal, which can treat 500 Nm^3/hr of flue gas from an iron-ore sintering machine. Using this experience, SHI has developed an SCR process with a moving bed.

A flowsheet of the process for boiler flue gas is shown in Figure 4-73. A catalyst is moved downward in the reactor, discharged from the reactor, screened to remove particulates and returned to the reactor. The catalyst, based on ferrite, is a 7 mm sphere, has a surface area of over 10 m^2/gram and has a crushing strength of more than 15 kg per granule. No attrition has been observed during the operation of the moving bed.

TABLE 4-18. INVESTMENT AND ANNUALIZED COSTS (MITSUI TOATSU CHEMICAL)

	Clean Gas	Dirty Gas
Capacity		
(Nm^3/hr)	200,000	200,000
(MW)	72	68
Fuel	LPG	Heavy Oil
Gas Temperature (°C)	250-350	350
NO_x Removal (percent)	90	90
Inlet NO_x (ppm)	100	100
Inlet SO_x (ppm)	1	300
Inlet Particulates (mg/Nm^3)	1	200
Investment Cost[a]		
(millions of yen, $5000)	800	1000
(yen/kW, $0.005/kW)	11,000	14,710
Annualized cost (yen/hr, $0.005/hr)		
Fixed Cost	15,000	18,750
Variable Cost	11,000	12,600
Total Cost	26,000	31,350
Total Cost		
(yen/t fuel, $0.005/t fuel)	1690	2005
(yen/kW, $0.005/kW)	0.36	0.43

[a] Including catalyst.

[b] For 8000 hours; yearly operation.

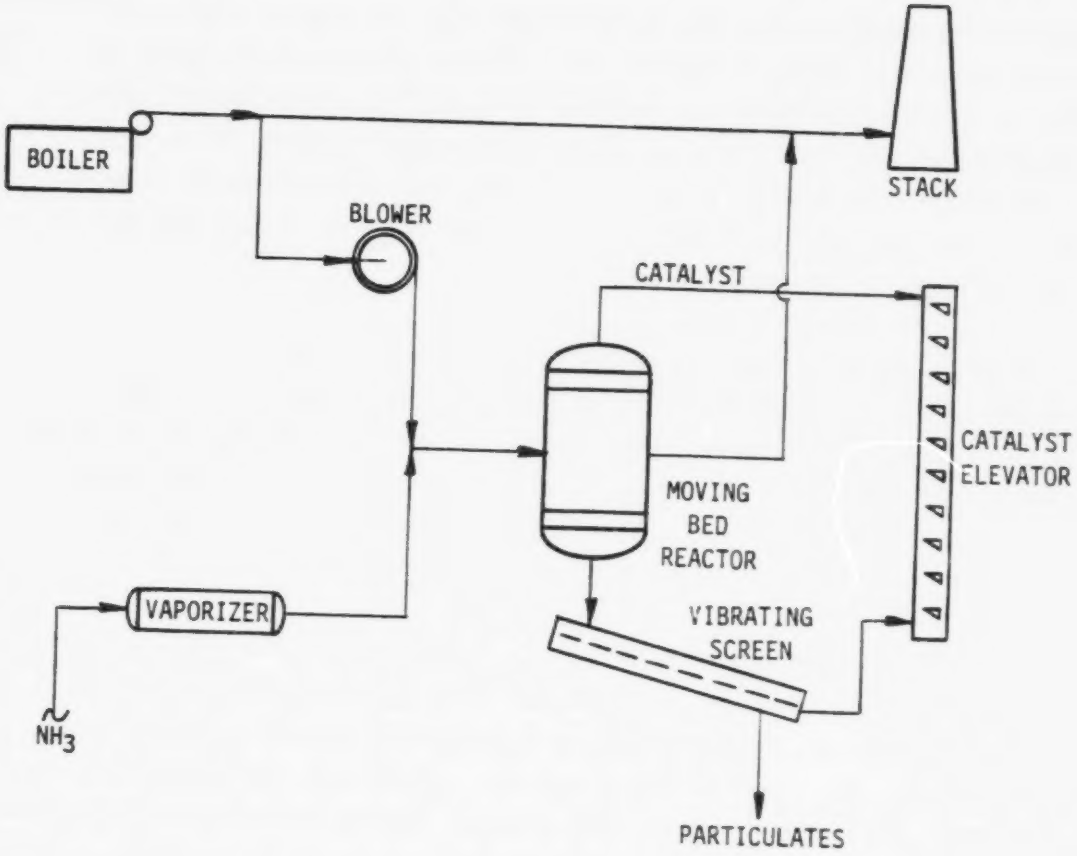

BOILER
STACK
BLOWER
CATALYST
CATALYST
ELEVATOR
MOVING
BED
REACTOR
VAPORIZER
VIBRATING
SCREEN
NH3
PARTICULATES

Figure 4-73. Flowsheet of Sumitomo Heavy Industry SCR process for boiler flue gas.

Figure 4-74 shows results of tests with a gas containing about 200 ppm NO_x, 450 ppm SO_x, and 150 mg/Nm^3 particulates. About 95 percent of the NO_x was removed at 350°C, an NH_3/NO_x mole ratio of 1.0, and an S/V of 5000 hr^{-1}. Relations between the inlet NH_3 concentration and the removal ratio and ammonia leakage is shown in Figure 4-75. The gas for the tests shown in Figure 4-75 contained about 130 ppm NO_x, 450 ppm SO_2, and 150 mg/Nm^3 dust. Normally an NH_3/NO_x mole ratio of 1.0 is used at 350°C and an SV of 5000 hr^{-1} to remove more than 90 percent of the NO_x and to keep ammonia leakage below 10 ppm. Usually 70-80 percent of the particulates in the flue gas is also removed by the catalyst bed.

It had been found that the activity of the ferrite catalyst is decreased by the presence of SO_x below 350°C. Sulfate deposits on the catalyst but it can be removed and activity restored by heating the catalyst at 700°C. The catalyst, with repeated thermal regeneration, is estimated to have a life of about 1 year. Recently SHI developed an SO_x-resistant catalyst based on TiO_2 which requires no thermal regeneration.

Based on the experience of operating the prototype FGD plant, SHI has designed a standard size reactor which can treat about 62,000 Nm^3/hr gas. By stacking three reactors, as shown in Figure 4-76, 186,000 Nm^3/hr of gas can be treated. For a 500 MW coal-fired boiler, ten such combined units may be used. A hot electrostatic precipitator will be installed to reduce dust content 99 percent from 20 to 0.2 $gram/Nm^3$, which is an acceptable limit for the reactor.

Plant operating costs for NO_x removal are estimated by SHI as shown in Table 4-19. The plant cost ranges from 9600 to 13,000 yen/kW ($48 to $65/kW), depending on the plant size. The denitrification cost, including 7 years' depreciation, is 0.59-0.71 yen/kWhr ($0.0029-$0.0035/kWhr) for 8320 hours' yearly operation. The costs do not include the electrostatic precipitator.

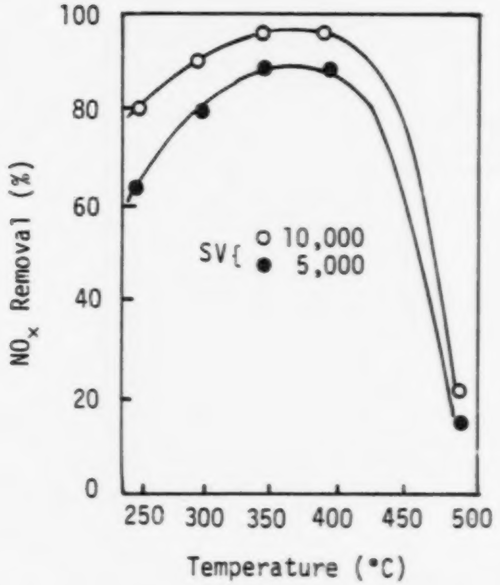


Figure 4-74. NO$_x$ removal versus temperature for the SHI process (NH_3/NO ratio = 1.0).

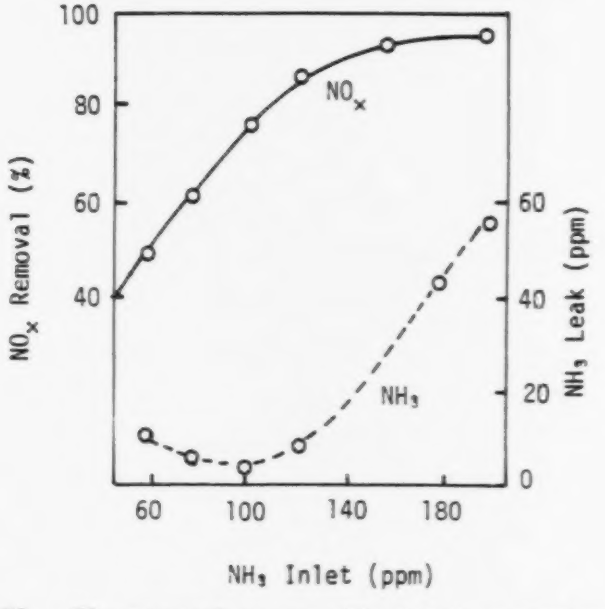


Figure 4-75. NO$_x$ removal versus NH_3 inlet concentration versus NH_3 leakage for the SHI process at 300 °C.

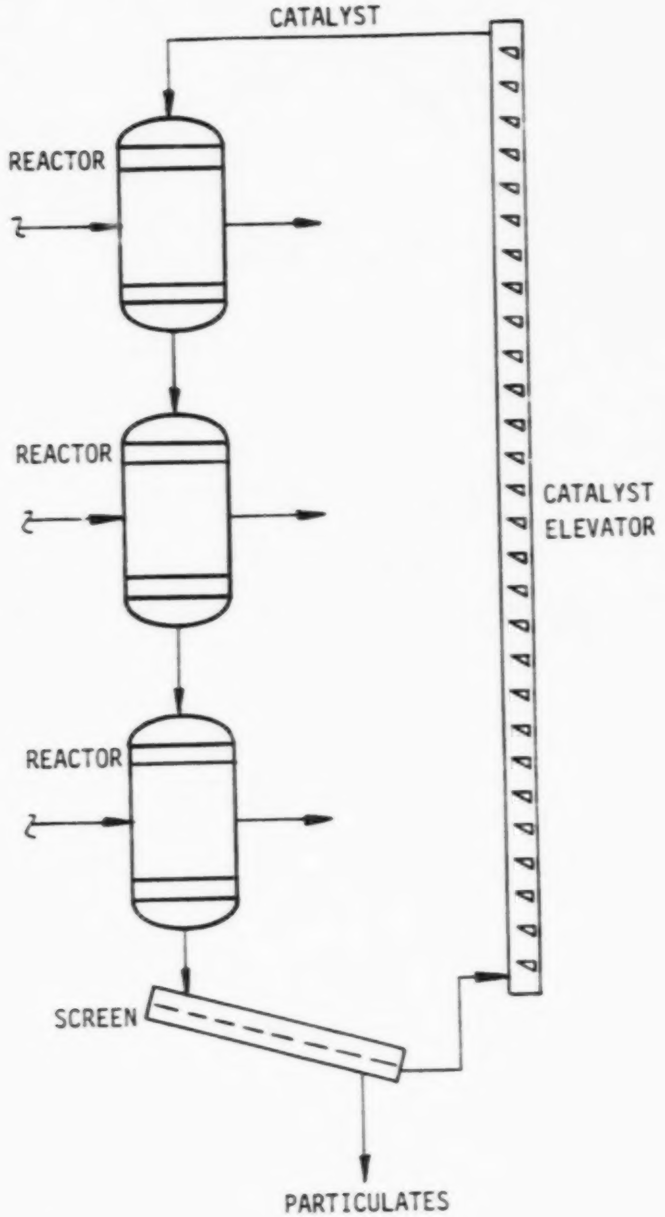

CATALYST
REACTOR
REACTOR
REACTOR
CATALYST ELEVATOR
SCREEN
PARTICULATES

Figure 4-76. Stacking of three SHI reactors to treat 186,000 Nm^3/hr of gas.

TABLE 4-19. SCR COST FOR FLUE GAS FROM OIL-FIRED BOILER, ESTIMATED BY SHI IN 1976[a]

	Flue Gas, Nm^3/hr (MW)		
	200,000 (65)	400,000 (130)	700,000 (230)
Capital Cost (millions of yen, $5000)[b]	850	1500	2210
Annual Cost (millions of yen, $5000)			
Fixed Cost[c]	166	281	431
Material Cost	161	321	562
Other	57	93	142
Total	384	695	1135
Annualized Cost[d]			
Yen/kl Oil ($0.005/kl)	3250	2940	2750
Yen/kWhr ($0.005/kWhr)	0.71	0.64	0.59

[a] Catalyst cost: 3000 yen/kg ($15/kg)
Catalyst life: 1 year
Power cost: 10 yen/kWhr ($0.05/kWhr)
NH_3 Cost: 39.7 yen/kg ($0.20/kg)
NO_x concentration: 200 ppm

[b] Including civil engineering work (foundation of reactor).

[c] 7 years' depreciation, 10 percent interest.

[d] 95 percent operation per year (8320 hours).

4.11.3 Nippon Kokan Iron Ore Catalyst Process[3]

Nippon Kokan (NKK), one of the largest steel producers, has developed a process that uses a certain kind of iron ore as SCR catalyst. NKK has performed pilot plant tests with 15,000 Nm^3/hr of flue gas from an iron-ore sintering machine (Figure 4-77). The flue gas contains about 200 ppm NO_x, 300 ppm SO_x, and 1.6 g/Nm^3 particulates. It is passed through an electrostatic precipitator and an FGD unit with the NKK ammonia-lime system. A portion of the desulfurized gas is used for the test after it has been heated by a heat exchanger and a heater to 350-400°C. Since the gas still contains considerable amounts of SO_x, particulates, and entrained mist, a moving bed reactor is used.

By using 1.2-1.5 moles of NH_3 for each mole of NO_x and an SV of 4700 hr^{-1}, 80-90 percent of the NO_x is removed. The NH_3 leakage is 50 ppm at 350°C and almost zero at 400°C; the iron ore also functions as an ammonia decomposition catalyst at 400°C or above.

Tests have shown that if the catalyst bed is not moved, the catalyst plugged up in a few weeks; the bed operated smoothly if it is moved. The iron ore catalyst reacts with SO_x to form a powdery sulfate. The iron ore catalyst discharged from the reactor is screened and returned to the reactor. The iron ore fines containing the sulfate are returned to the sintering machine.

Iron ore is cheap and the process is useful for steel plants. Since the iron ore contains small amounts of potassium and chlorine and the gas from the sintering machine often contains an appreciable amount of alkaline chloride vapor which tends to deposit on the SCR catalyst even in a parallel flow type reactor, the iron ore catalyst may be more suitable for treatment of such dirty gas. It need not be regenerated and is returned to the sintering machine when contaminated. The largest disadvantage of the process is that a considerable amount of energy is required for heating the

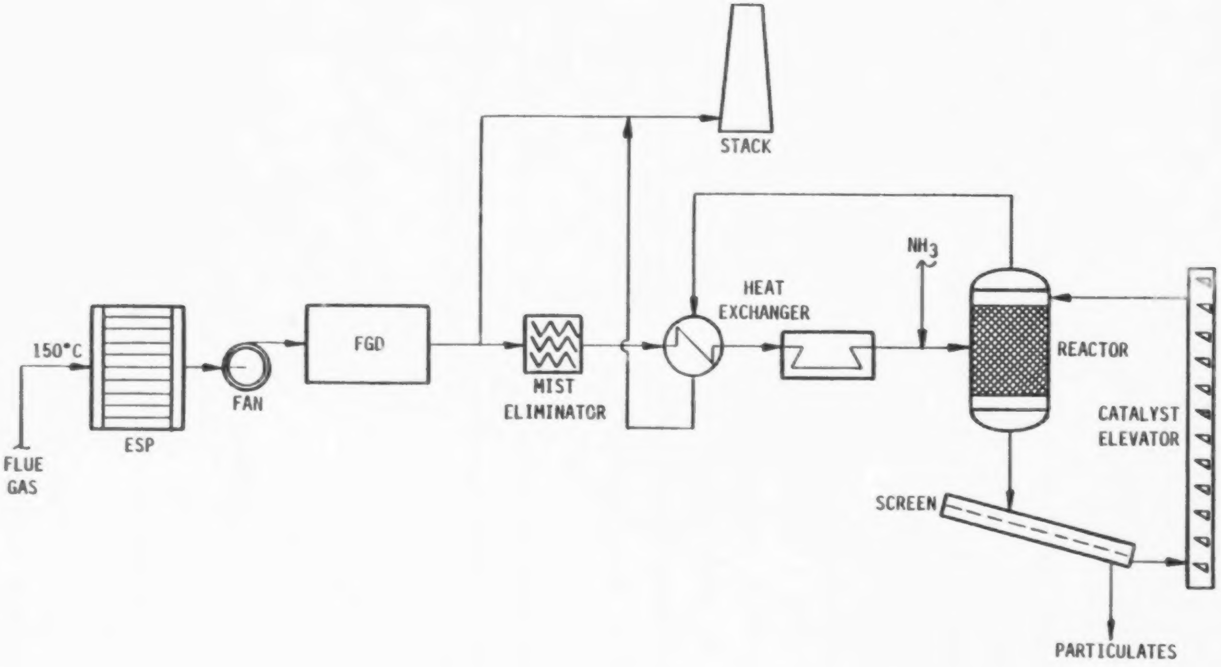

STACK
NH$_3$
HEAT EXCHANGER
150°C
FGD
REACTOR
FAN
MIST ELIMINATOR
CATALYST ELEVATOR
FLUE GAS
ESP
SCREEN
PARTICULATES

Figure 4-77. Flowsheet of NKK process for treating the flue gas from an iron-ore sintering machine.

the gas to 350-400°C. With a low-temperature catalyst such as the one developed by JGC (4.4.6), the energy requirement would be considerably lowered.

4.11.4 Mitsubishi Kakoki Kaisha (MKK) Process

Mitsubishi Kakoki Kaisha (MKK) has constructed several small commercial SCR plants as shown in Table 3-2. MKK initially used a ring shaped "Sarc" catalyst produced by Santetsu Kagaku from ferric oxide. This catalyst, however, is poisoned by SO_x-rich gas when used below 450°C. In the Kawasaki plant, Nippon Yakin, an improved type of catalyst, Sarc-SL, made from Fe_2O_3, TiO_2 and an additive, has been used. The NO_x removal performance is shown in Figure 4-78. The catalyst is actually used at around 350°C and an SV of 3000 hr^{-1} to remove 90 percent of the NO_x in flue gas from a high sulfur oil. In other plants, a TiO_2-based ring shaped catalyst produced by Catalyst and Chemicals (Section 3.4.2) has been used at an SV of 7000 hr^{-1}. No details of the plants have been disclosed.

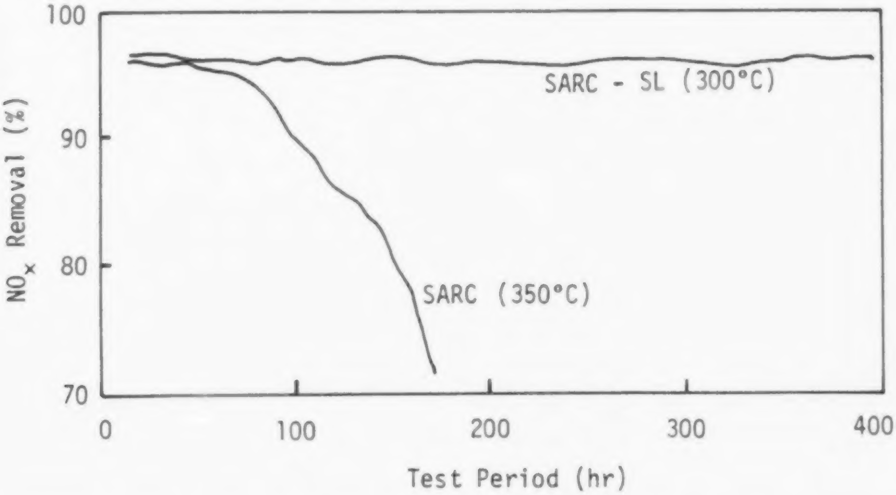


Figure 4-78. NO_x removal efficiency of MKK catalyst used for SO_2-rich gas at Nippon Yakin.
Note: SO_2 = 2000 ppm, NO = 200 ppm, O_2 = 8 percent, SV = 5000 hr^{-1}, NH_3/NO = 1.2

4.11.5 Kawasaki Heavy Industries

Kawasaki Heavy Industries has used various types of catalysts--sphere, pellet, plate, tube, and honeycomb--on SCR with flue gases from oil and coal fired boilers. Some of the results for flue gases from oil-fired boilers are shown in Figure 4-79. It is said that a tubular catalyst gave the best result for flue gas from coal with a full particulate load, but no details have been disclosed.

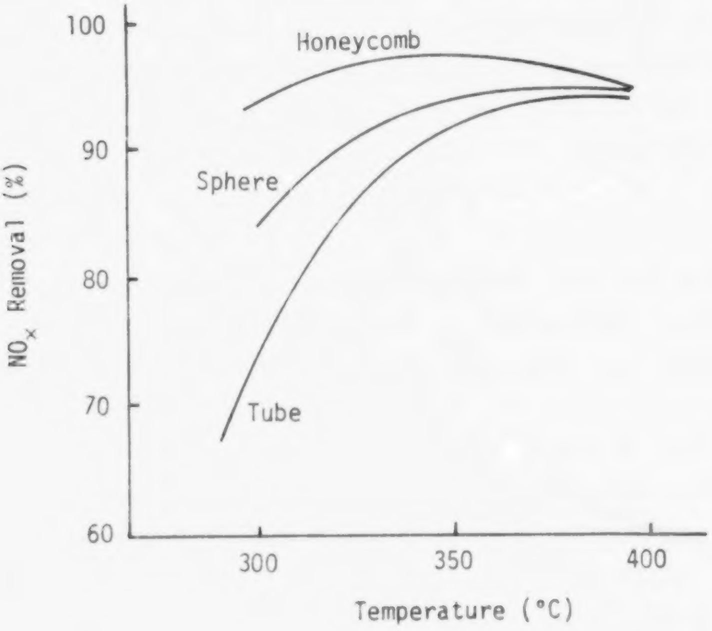


Figure 4-79. NO_x removal efficiency of KHI catalysts used for flue gas from oil-fired boilers.
Note: NO_x = 200-300 ppm, SO_x = 800 ppm, Particulates = 200 mg/Nm^3 for honeycomb and tube, 20 mg/Nm^3 for sphere, NH_3/NO = 1.0

4.11.6 Asahi Glass Process

Asahi Glass Co., the largest glass producer in Japan, has tested SCR in a prototype plant which can treat 70,000 Nm^3/hr of flue gas from a glass melting furnace. The gas contains 500-700 ppm NO and 300-500 ppm SO_2. A granular catalyst and intermittent moving bed developed by Asahi Glass have been used.

Since the gas contains not only solid particulates but also a considerable amount of sodium sulfate vapor which tends to condense on the catalyst and poison it, a catalyst carrier made of sintered MgO (periclase) is used. The periclase is fairly resistant to the poisoning. The carrier is quite strong and undergoes virtually no attrition in the moving bed. On the other hand, it has a relatively small surface area and is limited to a low SV. By treating the gas with about 1.1 mole of NH_3 for 1 mole of NO_x, 90-95 percent of the NO is removed at 350-400°C and an SV of 1500-2000 hr^{-1}

The catalyst has been water-washed once every month or two to remove sodium sulfate and particulates, and has been reused after the base metal catalyst component has been added. The life of the carrier is about 1 year.

Although over 90 percent of the NO_x can be removed, the process is troublesome and costly due to interference by sodium vapor. This interference can not be avoided even with a parallel passage reactor or honeycomb type catalyst. There is presently no plan to install a commercial plant for removing the NO_x from flue gas of a glass melting furnace.

4.12 REFERENCES

1. Inaba, H., Catalytic Reduction with Ammonia. Kaikan to Sochi, February 1977. In Japanese; same as Reference 8 of Chapter 3.

2. Miyata, K., Paranox Process Flue Gas Denitrification Plant. Haikan to Sochi, February 1977. In Japanese.

3. Same as Reference 4 of Chapter 1.

4. Atsukawa, M., *et al.*, Development of NO_x Removal Processes with Catalyst for Stationary Combustion Facilities. Mitsubishi Juko Giho, Vol. 13, No. 2, 1976. In Japanese.

5. Atsukawa, M., *et al.*, Development of Parallel Flow Type NO_x Removal Systems Using Plate Type Catalyst. Mitsubishi Juko Giho, Vol. 14, No. 2, 1978. In English.

6. Faucett, H. L., J. D. Maxwell, and T. A. Burnett, Technical Assessment of NO_x Removal Processes for Utility Application. EPRI AF-568, EPA-600/7-77-127, November 1977. In English.

7. Removal of NO_x by Dry Process. Mitsui Zosen Giho, No. 100, 1978. In Japanese.

SECTION 5

SELECTIVE NONCATALYTIC REDUCTION (SNR)

5.1 INTRODUCTION

It has long been known that NH_3 rapidly reacts with NO at around 1000 °C to form N_2 and H_2O. The reaction is an undesirable side reaction in the production of NO from NH_3 by catalytic oxidation at a nitric acid plant (Equation 5-1). Recent studies have shown that a small amount of O_2 is necessary for the reaction. Therefore, the reaction may be expressed by Equation 5-2:

$$6NO + 4NH_3 = 5N_2 + 6H_2O \qquad (5\text{-}1)$$

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad (5\text{-}2)$$

Nippon Kokan (NKK) in 1970 applied for a patent for a selective noncatalytic reduction (SNR) denitrification process in which ammonia is injected into flue gas above 600°C without a catalyst. Since the reaction of NH_3 with NO had been known, NKK claimed the use of a refractory structure to promote the mixing of NH_3 with flue gas. Rapid good mixing is a key point of the process.

A few years later, Exxon and Mitsubishi Chemical Industries (MCI) independently started working on a noncatalytic ammonia injection process and both applied for a patent, Exxon a little earlier than MCI. Exxon's patent includes the use of water-cooled ammonia injection nozzles to minimize the thermal decomposition of ammonia prior to the reaction with NO_x and also the use of hydrogen to lower the reaction temperature. All of the patents are now pending.

MCI, however, has made large scale tests at its own plants after obtaining a license from Exxon. Table 5-1 presents major SNR plants. Mitsubishi Heavy Industries (MHI) worked with MCI and recently completed a large test unit at Chita Power Station of Chubu Electric which can treat flue gas from a 375 MW utility oil-fired boiler.

Tonen Technology, a subsidiary of Toa Nenryo, has also obtained a license from Exxon, conducted large scale tests, and constructed medium-size commercial SNR plants (Table 5-1).

All of those units remove 40-60 percent of NO_x using 1-2 moles NH_3 to 1 mole NO_x. In addition, Mitsubishi Kakoki Kaisha has built many small SNR units (3000-6000 Nm^3/hr) to treat flue gas from heating furnaces. Although the removal ratio is not as high as by SCR, SNR is simple, less expensive, and useful for gas sources for which a high NO_x removal ratio is not needed.

Laboratory tests on SNR have been carried out by many researchers. Some results of the tests are compared in Figure 5-1. All tests indicate a maximum removal efficiency between 900 and 1050°C. Over 80 percent efficiency was obtained in laboratory tests in which NO and NH_3 were mixed and reacted in a silica tube. Tests by Exxon and MCI (curves 1 and 2) gave particularly high efficiency presumably because of the use of a large amount of NH_3 by Exxon and relatively long reaction time by MCI. Tests by CRIEPI (curve 5) using a small oil-fired furnace (700-800 Nm^3/hr of flue gas) gave maximum 45 percent removal which is close to the efficiency obtained at large scale plants.

Factors affecting NO_x removal efficiency, reaction mechanism, and operation of large scale plants will be described.

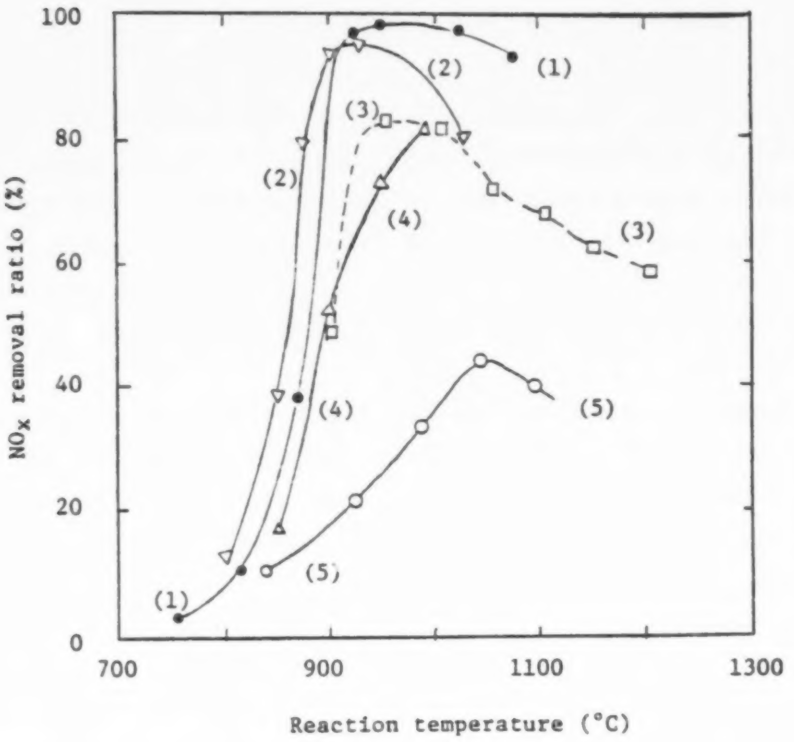
TABLE 5-1. LARGE SNR INSTALLATIONS (THERMAL DENO$_x$)

Process Supplier	User	Plant Site	Gas Source	Fuel	Gas Treated (Nm^3/hr)	Date of Start	Notes
MCI[a]	MCI	Mizushima	Industrial Boiler	Low-S Oil	540,000	1975	For test
MHI[b]	Chubu Electric	Chita	Utility Boiler	Low-S Oil	1,036,000	Feb 1977	Continuous operation
TT[c]	Mitsui Petrochemical	Chiba	Industrial Boiler	Naphtha	120,000	Dec 1975	Occasional operation
TT	Tonen Sekiyu Kagaku	Kawasaki	Industrial Boiler	Low-S Oil, Gas	423,000	Oct 1976	Emergency use
TT	Tonen Sekiyu Kagaku	Kawasaki	Industrial Boiler	Low-S Oil, Gas	423,000	July 1977	Emergency use
TT	Kyokyto Petroleum	Chiba	Pipistill Furnace	Low-S Oil, Gas	160,000	Oct 1977	Emergency use
TT	Toa Nenryo	Kawasaki	CO Boiler		314,000	Mar 1978	Emergency use
TT	Toa Nenryo	Kawasaki	Pipistill Furnace	Low-S Oil, Gas	254,000	Mar 1978	Emergency use

[a] Mitsubishi Chemical Industries.

[b] Mitsubishi Heavy Industries.

[c] Tonen Technology.



Researcher	Reactor	NO (ppm)	NH_3 (ppm)	O_2 (%)	Reaction Time (sec)
(1) Exxon[1]	Silica Tube	826	2540	4.6	0.13-0.17
(2) MCI	Silica Tube	200	400	2.0	0.4
(3) Chubu Electric	Silica Tube	200	240	1.0	0.2
(4) Okayama University[2]	Silica Tube	500	667	1.0	0.1-0.13
(5) CRIEPI[3]	Oil Furnace	225	225	1.0	0.11

Figure 5-1. Results of laboratory tests of SNR by five research organizations.[2]

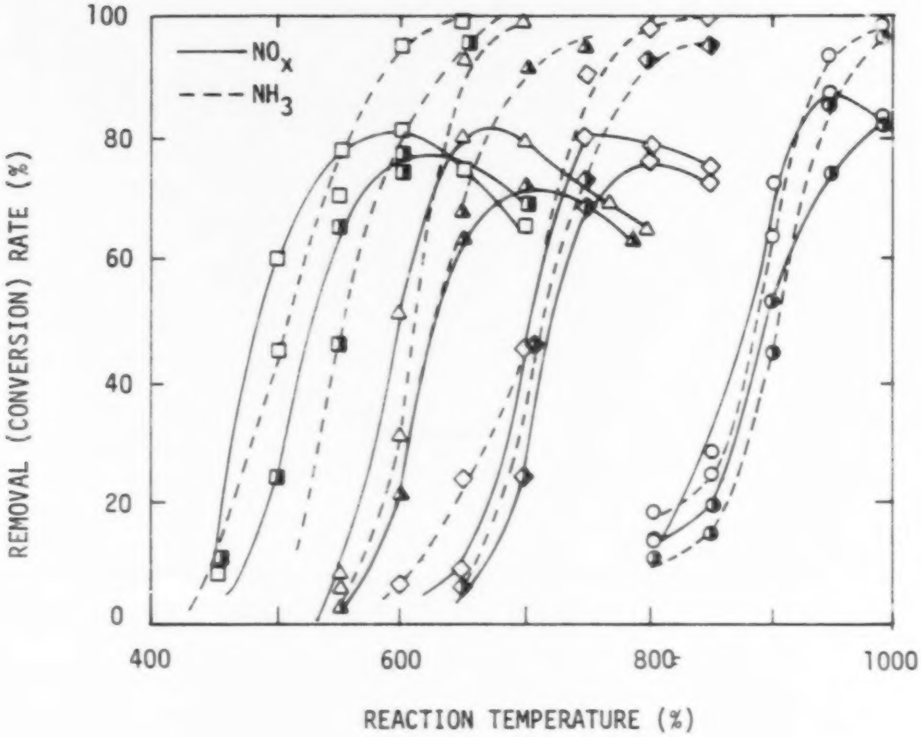
5.2 LABORATORY TESTS AT OKAYAMA UNIVERSITY

S. Kasaoka, Okayama University, has performed extensive laboratory tests on the noncatalytic reduction process.[2] In the tests, he used a 13 mm diameter silica tube placed in a tubular furnace, and passed a composite gas through the tube at a rate of 1 normal liter per minute. Retention time of the gas at reaction temperature was 0.10-0.13 second. Both the inlet and outlet NO and NH_3 concentrations were measured.

Figure 5-2 shows the removal rate of NO and the conversion rate of NH_3 when a gas containing 500 ppm NO and 667 ppm NH_3 (NH_3/NO mole ratio = 1.33) with or without H_2 or H_2O was treated at temperatures between 450 and 1000 °C. For a gas without H_2, the optimum reaction temperature was 950-1000°C. At 1000°C, about 80 percent of NO_x and 95 percent of NH_3 were removed, indicating that less than about 100 ppm NO_x and 30 ppm NH_3 were present in the outlet gas. Addition of H_2 lowered the optimum reaction temperature as claimed by Exxon and also tended to lower the NO_x removal efficiency. Presence of H_2O lowered both NO_x removal and NH_3 conversion rates.

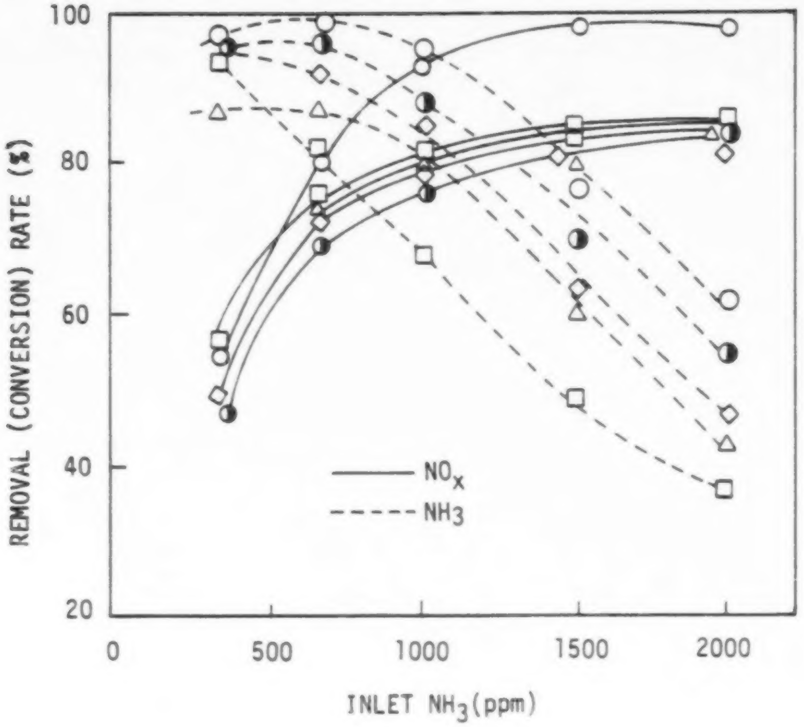
Figure 5-3 shows that the use of a larger amount of NH_3 gives a higher NO_x removal ratio and larger amount of ammonia leakage (NH_3 in outlet gas). At 1000°C with 1000 ppm NH_3 (NH_3/NO_x ratio 2) and without H_2, the NO_x removal rate exceeded 90 percent and the NH_3 conversion rate was 94 percent (NH_3 leakage was about 60 ppm). Reaction at lower temperatures using H_2 gave a smaller NO_x removal rate with more NH_3 leakage.

Figure 5-4 shows the effect of O_2 concentration on NO_x removal and NH_3 conversion. The optimum O_2 concentrations for NO_x removal were about 3 percent for a gas with 5 percent H_2 and about 1 percent for a gas with 1 percent H_2. The optimum O_2 concentration for a gas without H_2 was below 1 percent (not shown in Figure 5-4). Excessive O_2 concentration lowered the removal efficiency although it also lowered the amount of NH_3 leakage.



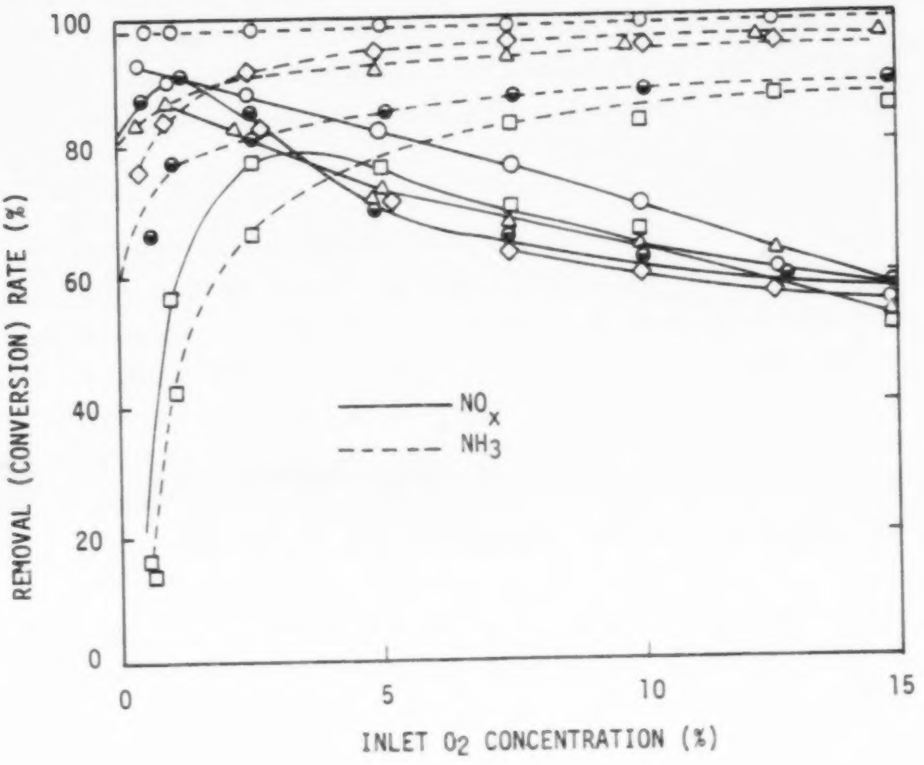
KEY	NO_x (ppm)	NH_3 (ppm)	O_2 (%)	H_2 (%)	H_2O (%)
○	500	667	5	0	0
◑	500	667	5	0	10
◇	500	667	5	1000	0
⬗	500	667	5	1000	10
△	500	667	5	5000	0
▲	500	667	5	5000	10
□	500	667	5	50000	0
◨	500	677	5	50000	10

Figure 5-2. Effects of H_2 and H_2O concentrations on NO_x removal rate and NH_3 conversion rate at a reaction time of 0.1-0.13 seconds, according to tests at Okayama University.



MARKS	INLET GAS COMPOSITION					REACTION TEMP (°C)
	NO(ppm)	H_2(ppm)	O_2 (%)	H_2O (%)	N_2	
○	500	0	5	10	BALANCE	1000
△	500	1000	5	10	"	800
◑	500	3000	5	10	"	750
◇	500	5000	5	10	"	700
□	500	50000	5	10	"	600

Figure 5-3. Effects of NH_3 and H_2 concentrations and reaction temperature on the NO_x removal rate and the NH_3 conversion rate with a reaction time of 0.1-0.13 second, according to tests at Okayama University.



MARK	INLET GAS COMPOSITION				REACTION TEMP. (C)
	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	H_2O (%)	
○	500	667	0	10	1000
△	500	667	1000	10	800
◇	500	667	5000	10	700
◒	500	667	10000	10	650
□	500	667	50000	10	600

Figure 5-4. Effect of O_2 concentration on the NO_x removal rate and the NH_3 conversion rate with a reaction time of 0.1-0.13 second, according to tests at Okayama University.

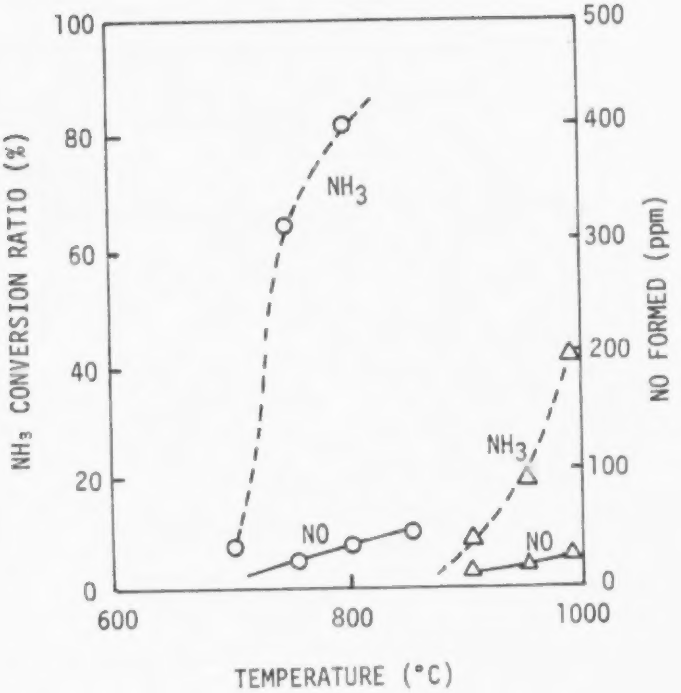
Figure 5-5 illustrates the thermal decomposition of NH_3 in a gas without NO. When H_2 was absent, NH_3 decomposed about 800°C forming a small amount of NO. H_2 promoted the decomposition of NH_3 and the formation of NO at a lower temperature. These results explain the effects of H_2 shown in Figure 5-2.

Figure 5-6 indicates the relationship of the reaction time to NO_x removal. Under appropriate conditions (950°C without H_2 and 750°C with 3000 ppm H_2), about 70-80 percent of the NO_x was removed within 1 second. A much longer reaction time was required at a lower temperature. In an actual boiler, the retention time of the gas in a suitable temperature range (for example, 950-1050°C without H_2 and 650-750°C with 3000 ppm H_2) may be less than 0.2 second. Therefore, it is important that NH_3 be introduced in a correct temperature zone and be mixed with the gas rapidly.

Figure 5-7 illustrates the relationship of reaction time to NH_3 conversion and NO formation for gases with different compositions at different temperatures. (NO was not present at first.) Under conditions suitable for NO_x removal, 950-1000°C without H_2, NH_3 decomposed rapidly; the amount of NO formed was small and did not increase at prolonged reaction time. At 700°C and 650°C in the presence of H_2, the NO concentration increased with prolonged reaction time.

5.3 STUDIES BY CRIEPI

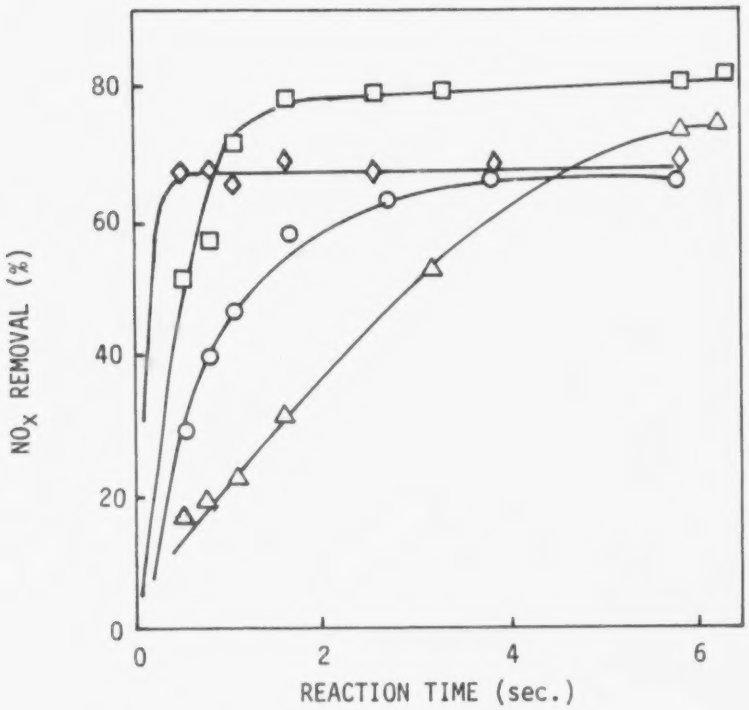
The Central Research Institute for Electric Power Industry (CRIEPI) has studied SNR to characterize the theoretical relationships of the associated reactions.[3] Since equilibrium constants and reaction rate constants of many of the reactions related to NO_x reduction are already known, Criepi calculated from those data the reaction rates for a gas containing 200 ppm NO, 1 percent O_2, and 11 percent H_2O. The results are shown in Figure 5-8. The gas composition is similar to that of flue gas from an oil-fired boiler.



INLET GAS COMPOSITION

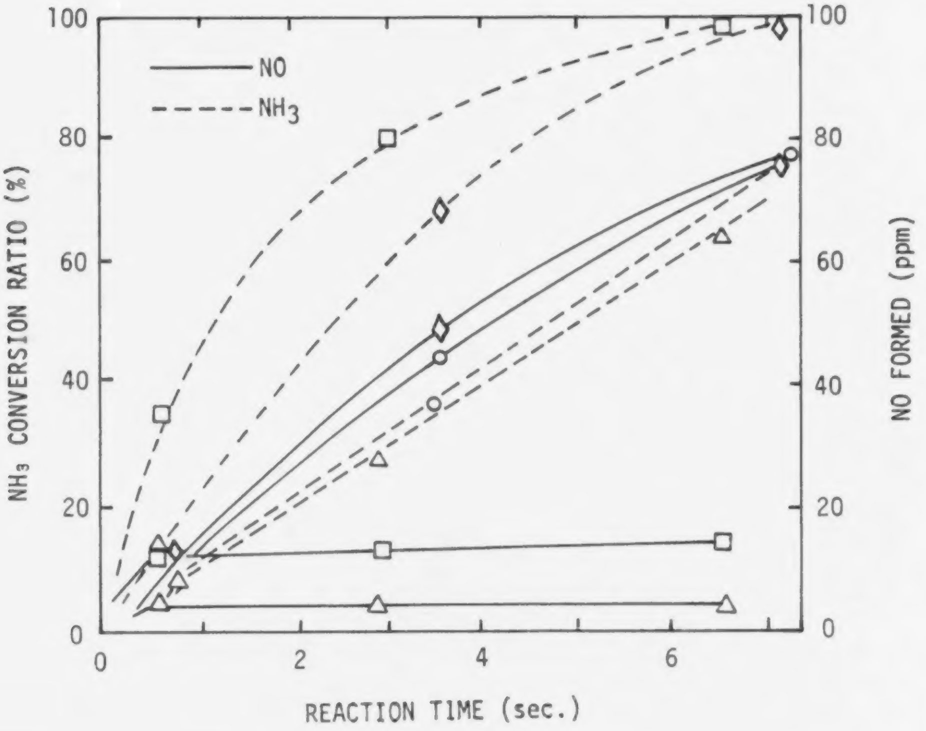
MARKS	NH_3(ppm)	H_2(ppm)	O_2(%)	H_2O(%)	N_2
○	667	3000	5	10	Balance
△	667	0	5	10	Balance

Figure 5-5. Effect of H_2 concentration on decomposition of NH_3 and formation of NO with a reaction time of 0.1-0.13 second, according to tests at Okayama University.



Marks	Composition of Inlet Gas						Reaction
	NO(ppm)	NH_3(ppm)	H_2(%)	O_2(%)	H_2O (%)	N_2	Temp. (°C)
□	500	667	0	5	10	Balance	950
△	500	667	0	5	10	"	850
◇	500	667	3000	5	10	"	700
○	500	667	3000	5	10	"	650

Figure 5-6. Effect of reaction time, temperature and gas composition on NO_x removal, according to tests at Okayama University.



Mark	Inlet Gas Composition					Reaction Temp. (°C)
	NH_3 (ppm)	H_2(ppm)	O_2 (%)	H_2O (%)	N_2	
□	667	0	5	10	Balance	1000
△	667	0	5	10	"	950
◇	667	3000	5	10	"	700
○	667	3000	5	10	"	650

Figure 5-7. Decomposition of NH_3 and formation of NO of different gases at different temperatures, according to tests at Okayama University.

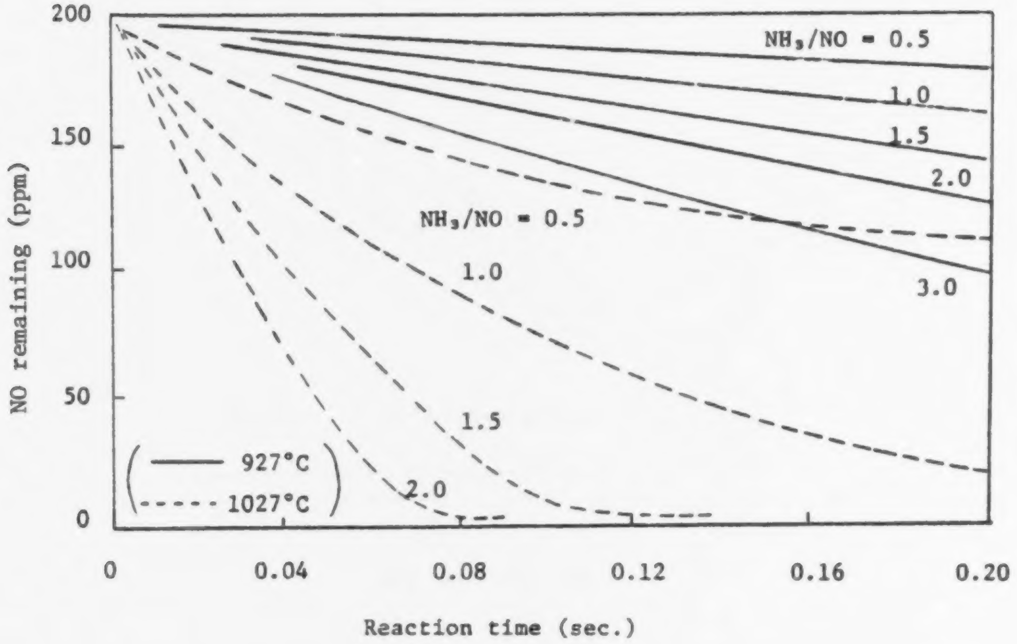


Figure 5-8. The effects of the NH_3/NO mole ratio and temperature on NO_x removal, according to CRIEPI studies.*

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* Calculated for a gas containing 200 ppm NO, 1 percent O_2 and 11 percent H_2O, similar to a gas from an oil-fired boiler.

Figure 5-8 indicates that 95 percent NO_x removal can be attained at 1027°C (1300°K) in 0.1 second with an NH_3/NO mole ratio of 1.5 and in 0.07 second with a ratio of 2.0. Those calculations were made assuming an ideal gas mixing which cannot be actually attained, particularly in large scale plants. Figures 5-9 and 5-10 show the conversion of NH_3 and formation of NO. Figure 5-10 indicates that the concentration of NO formed at 1027°C is only about 2 ppm and hardly increases at longer reaction time while much more NO is formed at higher temperatures.

Figure 5-10 does not agree well with Figure 5-7. This indicates that NO concentration exceeded 10 ppm within a second at 1000°C. The discrepancy may be due to the difference in O_2 concentrations--1 percent in Figure 5-10 and 5 percent in Figure 5-7--as well as to the difficulty of instantaneous and uniform heating and mixing of a gas.

Figure 5-11 (A-C) illustrates the effects of H_2 on the conversion of NH_3 and formation of NO and NH_3. The theoretical calculation shows that small amounts of NH_2, an unstable gas, form at the beginning of NH_3 conversion and that H_2 promotes the conversion of NH_3 and the formation of NO.

CRIEPI assumed that the following reactions would occur:

$$NH_3 + \tfrac{1}{4} O_2 = NH_2 + \tfrac{1}{2} H_2O \ (k = 1.2 \times 10^{-3} \text{ at } 700°C) \qquad (5\text{-}3)$$

$$NO + NH_2 = N_2 + H_2O \ (k = 7.9 \times 10^{25} \text{ at } 700°C) \qquad (5\text{-}4)$$

$$NH_3 + NO + \tfrac{1}{4} O_2 = N_2 + 1\tfrac{1}{2} H_2O \qquad (5\text{-}5)$$

$$H_2 + O_2 = H_2O + O \ (k = 1.8 \text{ at } 700°C) \qquad (5\text{-}6)$$

$$O + 2NH_3 = 2NH_2 + H_2O \qquad (5\text{-}7)$$

$$NH_3 + 2\tfrac{1}{2} O = NO + 1\tfrac{1}{2} H_2O \ (k = 9.4 \times 10^{39} \text{ at } 700°C) \qquad (5\text{-}8)$$

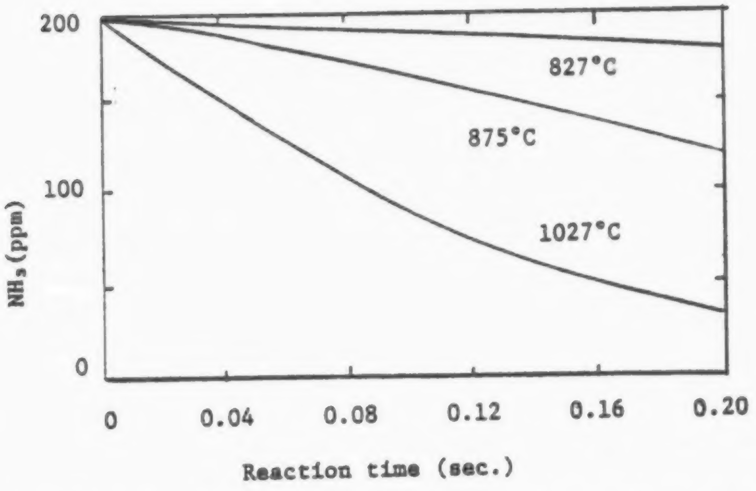


Figure 5-9. Decomposition of NH_3, calculated by CRIEPI.

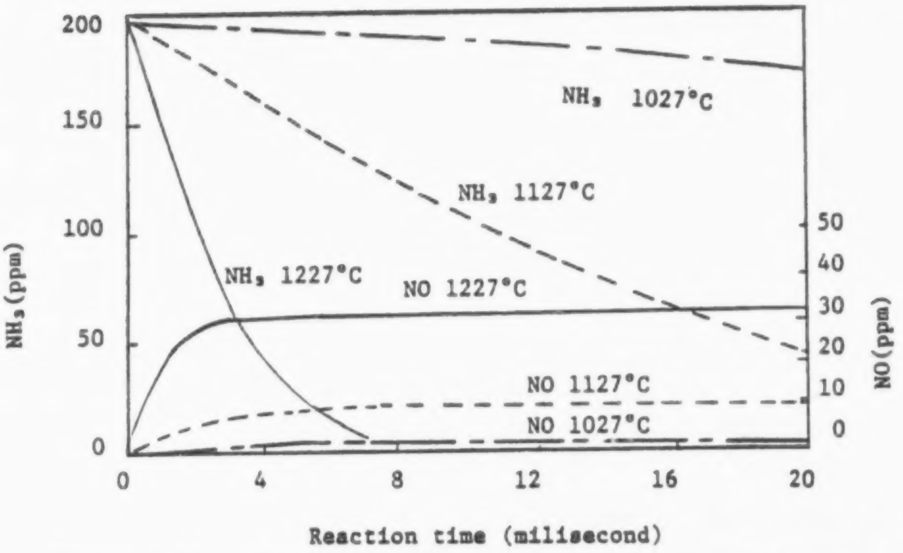


Figure 5-10. Effect of temperature on NH_3 conversion and NO formation, calculated by CRIEPI.

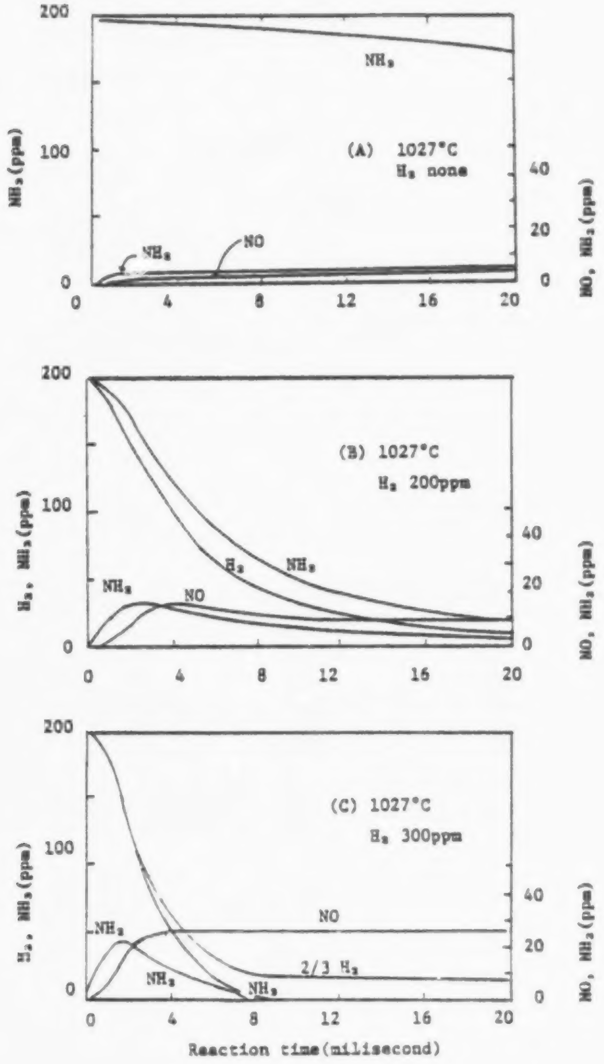
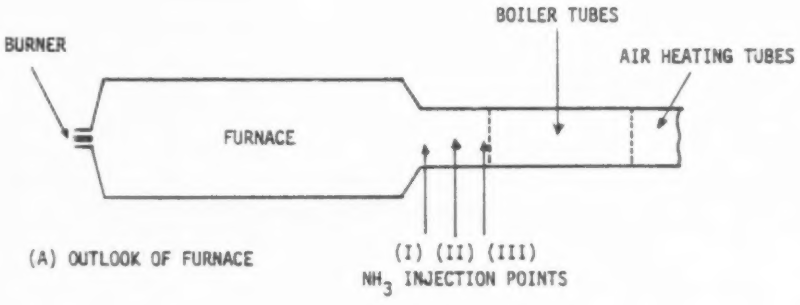
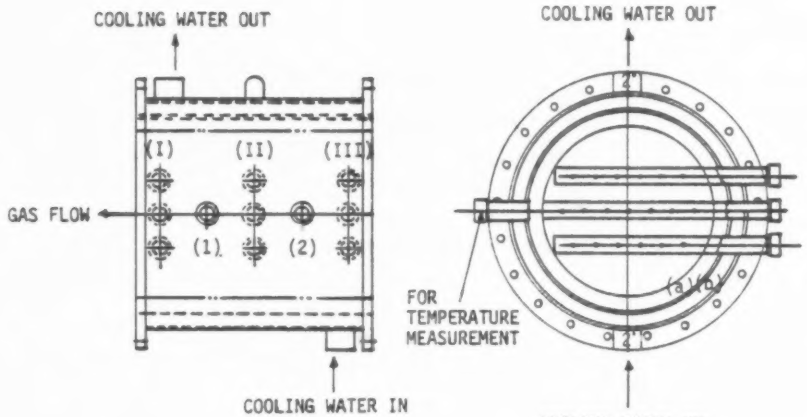


Figure 5-11. Effect of H_2 on NH_3 conversion and NO and NH_2 formation, calculated by CREIPI.


BURNER
FURNACE
BOILER TUBES
AIR HEATING TUBES
(I) (II) (III)
NH_3 INJECTION POINTS

(A) OUTLOOK OF FURNACE


COOLING WATER OUT
(I)
(II)
(III)
GAS FLOW
(1)
(2)
COOLING WATER IN
COOLING WATER OUT
2'
FOR TEMPERATURE MEASUREMENT
(a)
(b)
2'
COOLING WATER IN

(B) DETAIL OF NH_3 INJECTION POINTS (I,II,III) AND TEMPERATURE MEASURING POINTS (1,2.) (VIEW OF OPPOSITE SIDE OF THE FURNACE SHOWN IN A)

(C) NH_3 INJECTION NOZZLES
(3 NOZZLES WITH TOTAL 19 HOLES)
(CROSS SECTION OF FURNACE)
(a) REFRACTORIES
(b) COOLING WATER

Figure 5-12. Furnace and ammonia injection nozzles for SNR by CRIEPI (sizes are in mm).

NH_3 reacts only slightly with NO when O_2 is not present. It is assumed that reaction 5-3 occurs to form NH_3, which reactions with NO to form N_2 as shown by equation 5-4. The overall reaction is shown by equation 5-5. The equilibrium constant k of reaction 5-3, however, is very small at 700°C and thus reaction 5-5 does not proceed at 700°C.

When H_2 is added, reaction 5-6 occurs to form an oxygen radical which readily reacts with NH_3 to form NH_2. The NH_2 thus formed readily reacts with NO. The equilibrium constants for reactions 5-6, 5-7 and 5-4 are large enough for the reactions to proceed at 700°C. A portion of the oxygen radical reacts with NH_3 to form NO (reaction 5-8). Therefore the overall NO_x removal efficiency tends to be lowered by the addition of H_2 as already shown in Figure 5-2.

CRIEPI has made tests with a small oil-fired furnace about 1 meter in diameter, burning 50 liters/hr of oil, giving 700-800 Nm^3/hr gas as shown in Figure 5-12. Three ammonia injection points, I, II and III were used for tests. Three nozzles were placed in each point as shown in B and C of the figure. The three nozzles have a total of 19 holes with 1.1 mm diameter through which NH_3 or a mixture of NH_3 and H_2 was injected. The injection point I gives about 0.1 second reaction time of NH_3 with NO_x while the points II and III give less reaction time. The gas velocity at the injection points was about 4.6 m/sec at 1000°C.

Figure 5-13 shows the results of preliminary tests on the effect of water cooling of ammonia injection nozzles. By injecting 1 mole NH_3 to 1 mole NO_x from the injection point I, about 45 percent NO_x removal was attained when water-cooled nozzles were used but the results were poor without water cooling. This indicates that a large portion of NH_3 was decomposed at above 700°C in the tubes before it was mixed with flue gas. Water-cooled nozzles were used for other tests.

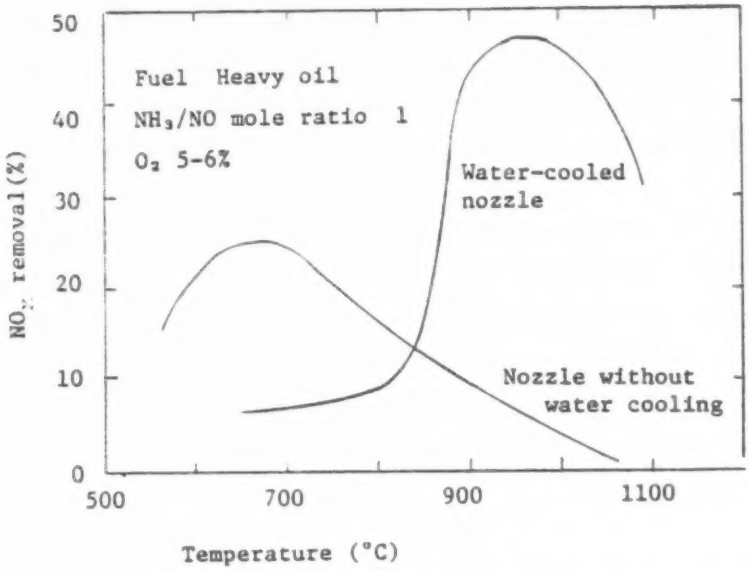


Figure 5-13. The effect of cooling the NH_3 injection nozzle on a small CRIEPI furnace.

Figure 5-14 shows that the removal efficiency was low when injection point II or III was used, indicating that the reaction time was too short. The injection point I was used for other tests.

Figure 5-15 indicates that removal was poor with flue gas from methanol burning. A high H_2O concentration of the burning gas may be one reason for the low removal efficiency (Figure 5-2). Figure 5-16 shows the results with flue gas from oil burning at different NH_3/NO and H_2/NO ratios. Addition of H_2 lowered the optimum reaction temperature as reported by Exxon. In all tests, the removal ratio did not exceed 50 percent even with 2 moles NH_3 for each mole of NO; presumably a good mixing and sufficient reaction time as was obtained in the laboratory cannot be achieved on a larger scale.

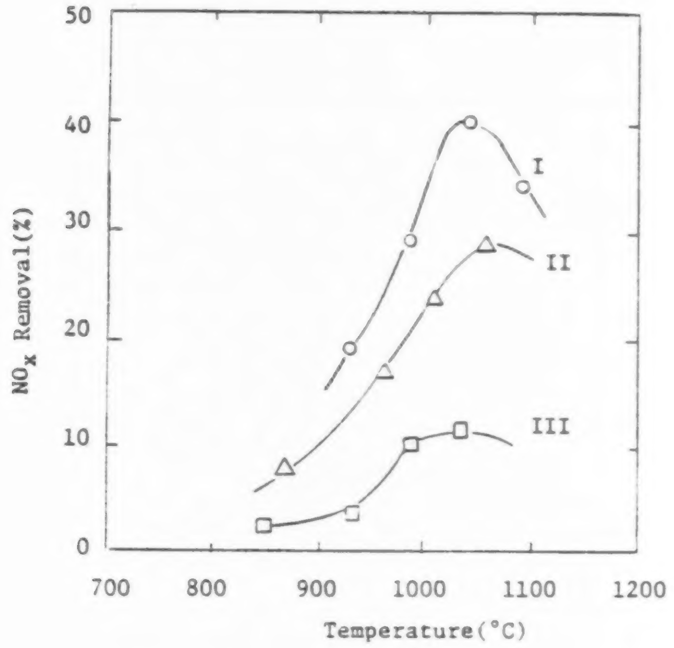


Figure 5-14. NO$_x$ removal by NH$_3$ injection at different points on a small CRIEPI furnace.*

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* Inlet NO$_x$ = 225 ppm
NH$_3$/NO$_x$ ratio = 1
O$_2$ = 1 percent

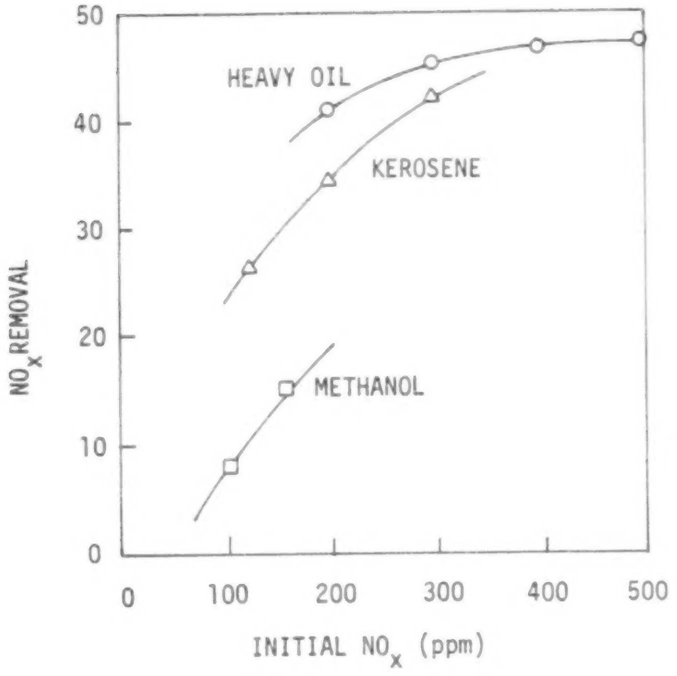


Figure 5-15. NO_x removal efficiency for the flue gas from the burning of several fuels in a small CRIEPI furnace.

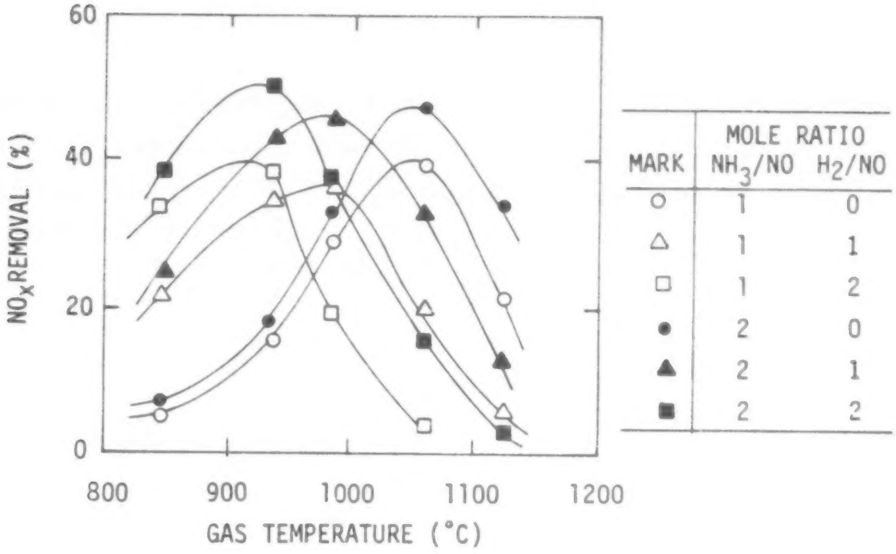


Figure 5-16. Effect of NH_3/NO mole ratio and H_2 addition on NO_x removal for the flue gas from oil burning in a small CRIEPI furnace.

CRIEPI detected minor amounts of cyanate in the gas after SNR. When 1 mole NH_3 was used to 1 mole NO_x, the amount of cyanate was close to that without ammonia injection. The amount of cyanate increased with the amount of ammonia but was still very low and may not be an environmental problem.

5.4 LARGE SCALE TEST OF SNR AT CHITA STATION, CHUBU ELECTRIC

5.4.1 Introduction

In 1977, Chubu Electric installed a full scale SNR test unit at Chita Station for the existing No. 2 boiler which burns a low sulfur oil. Before the installation, basic studies were made by Chubu Electric and also by MHI (Section 4.6), the constructor of the unit. The unit is the world's first full scale SNR plant for use on a utility boiler.

5.4.2 Basic Study by Chubu Electric[4]

Chubu Electric has made extensive laboratory tests on SNR using an apparatus as shown in Figure 5-17. Some of the test results are shown in Figures 5-18 - 5-21. Maximum NO_x removal was obtained at 950-1000°C (Figure 5-18). When 240 ppm of NH_3 was used for 200 ppm NO, 80 percent of the NO was removed at 1000°C with a reaction time of 0.2 second (Figures 5-18 and 5-19). The addition of H_2 or CH_4 shifted the optimum reaction temperature from 1000°C to about 800°C (Figures 5-20 and 5-21).

Figures 5-22 and 5-23 show the effects of temperature and NH_3/NO mole ratio on NO_x removal efficiency and NH_3 leakage. At 1100°C and 1200°C, both NO_x removal efficiency and NH_3 leakage are low. It is likely that a portion of the NH_3 is converted to NO at the high temperatures.

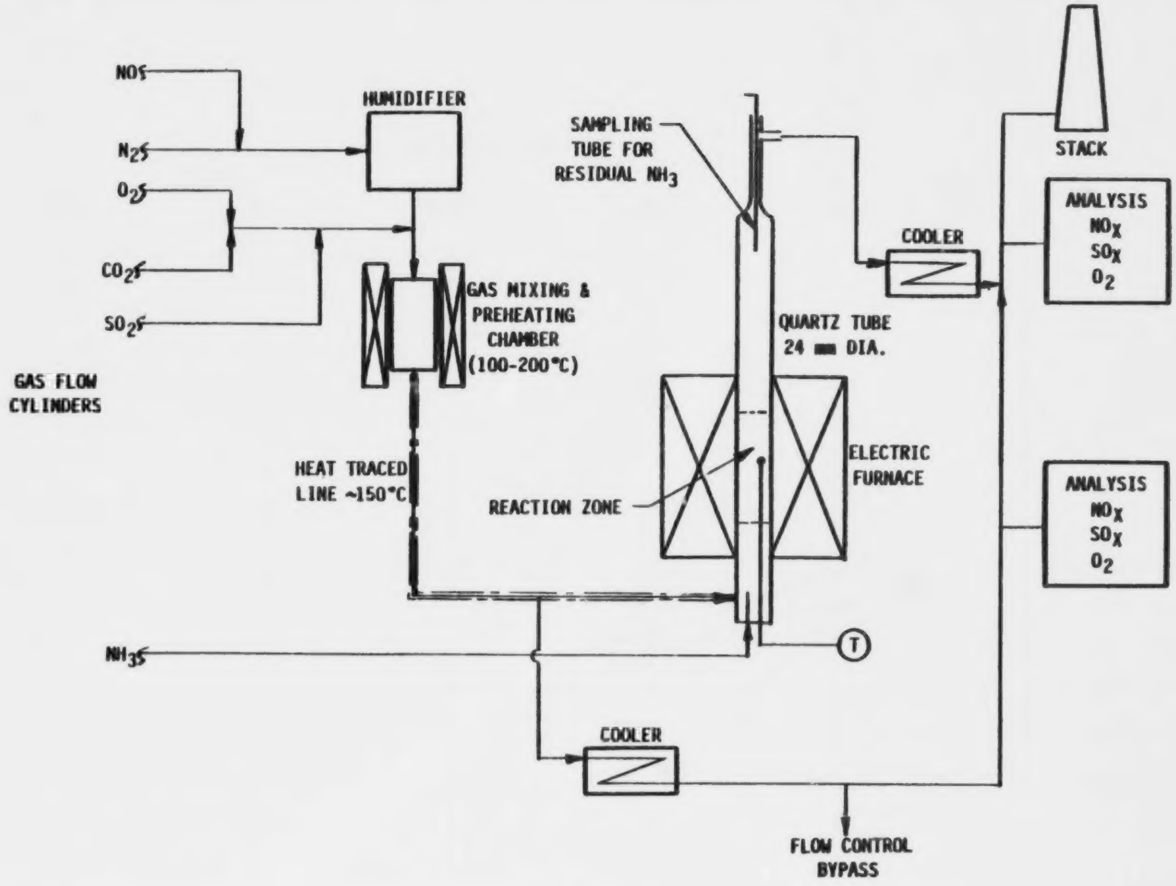

NO
HUMIDIFIER
N_2
O_2
CO_2
SO_2
GAS FLOW CYLINDERS
GAS MIXING & PREHEATING CHAMBER (100-200°C)
HEAT TRACED LINE ~150°C
NH_3
SAMPLING TUBE FOR RESIDUAL NH_3
QUARTZ TUBE 24 mm DIA.
REACTION ZONE
ELECTRIC FURNACE
T
COOLER
COOLER
FLOW CONTROL BYPASS
STACK
ANALYSIS NO_X SO_X O_2
ANALYSIS NO_X SO_X O_2

Figure 5-17. Schematic of experimental apparatus for Chubu Laboratory tests of SNR.

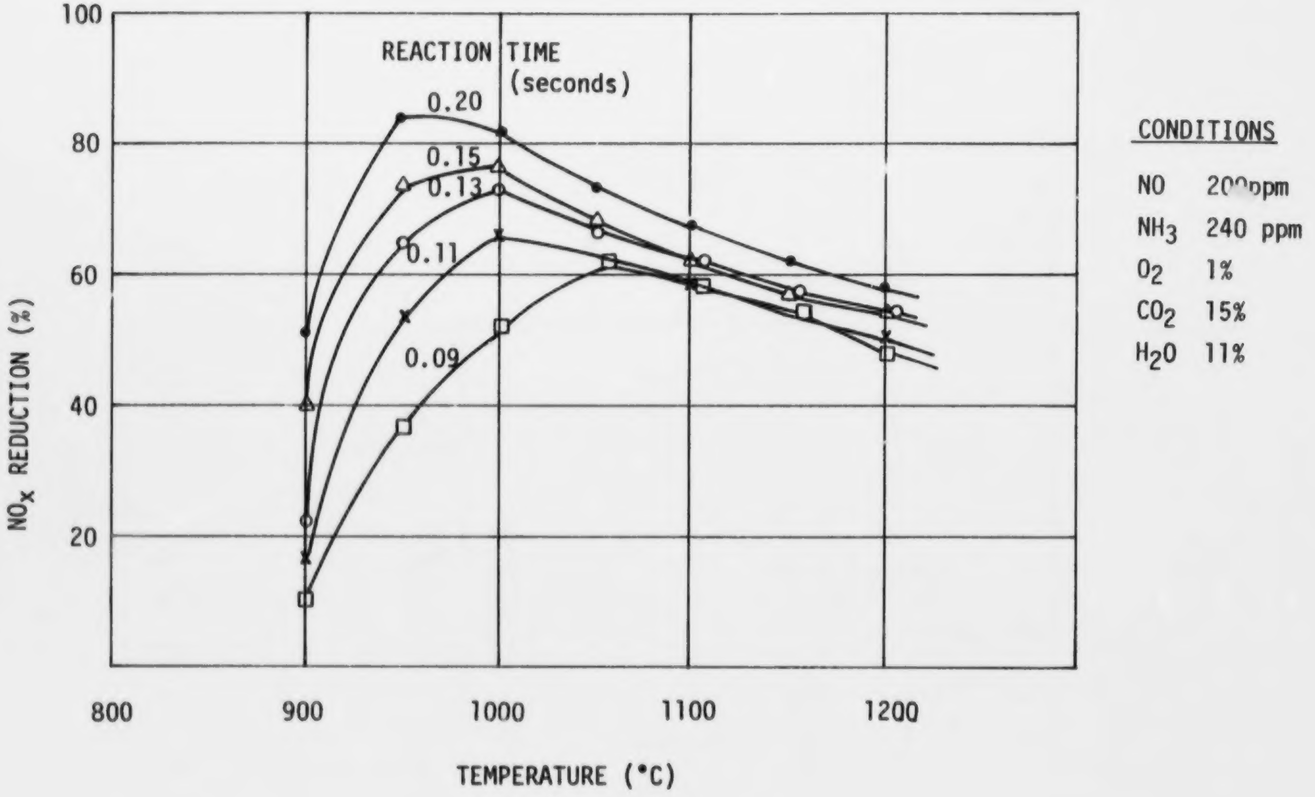


Figure 5-18. NO_x reduction versus reaction temperature with Chubu Electric's SNR.

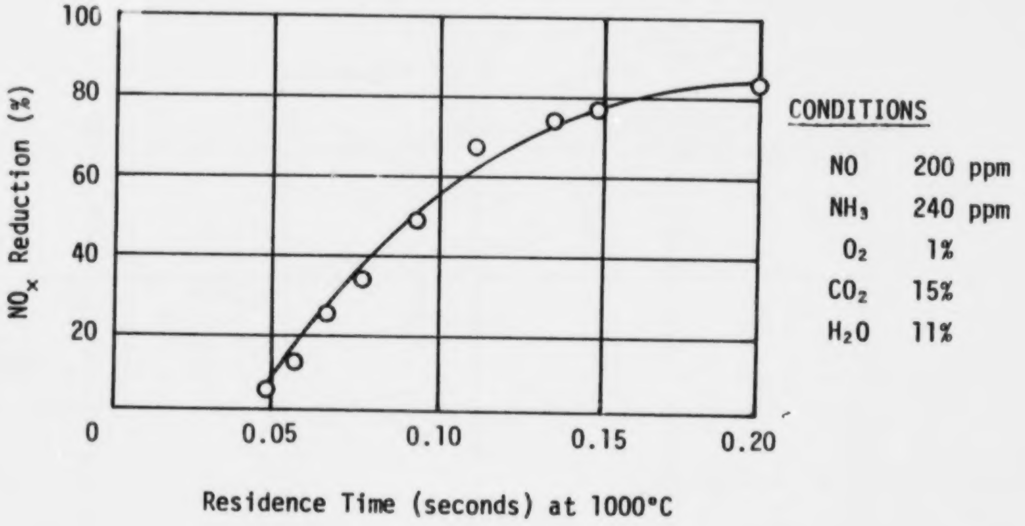


Figure 5-19. NO$_x$ reduction versus residence time in reaction zone with Chubu Electric's SNR.

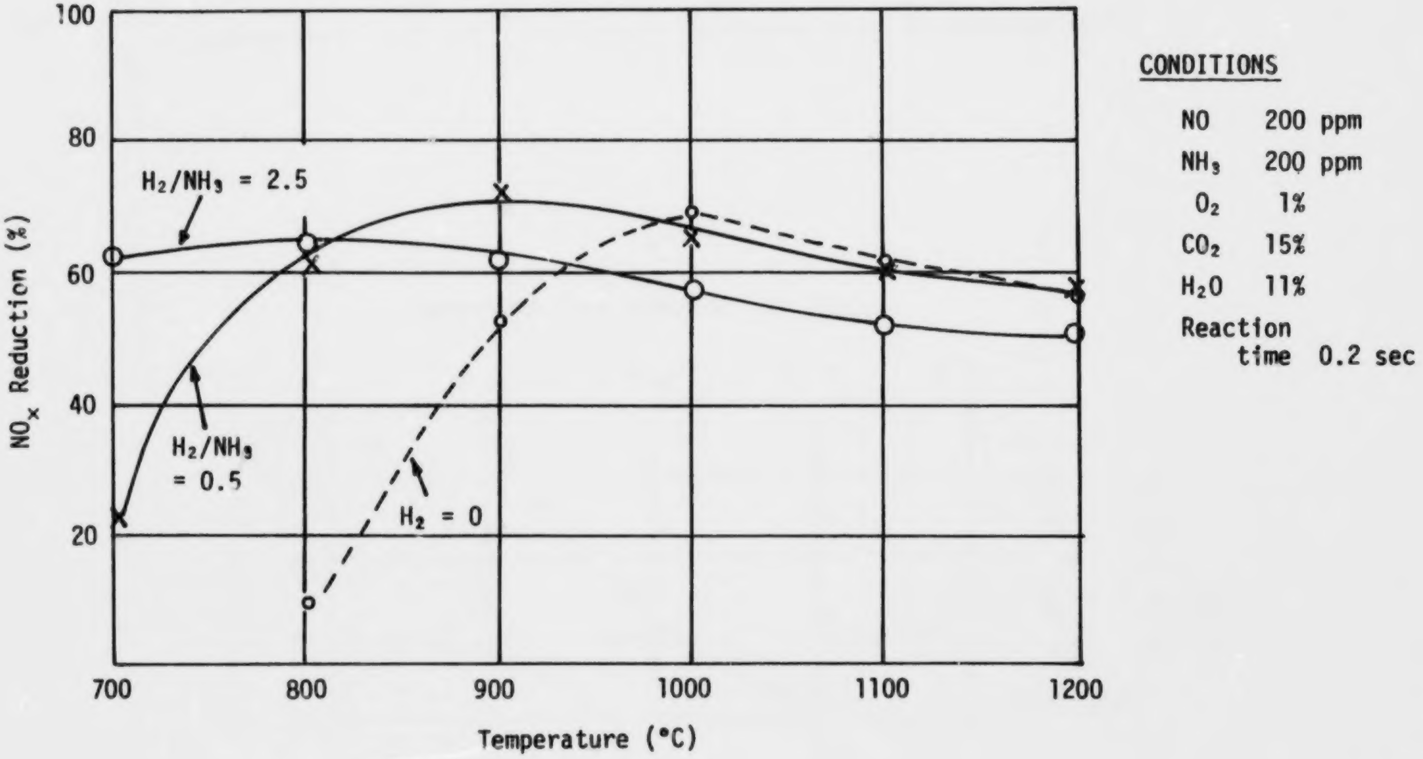


Figure 5-20. NO_x reduction versus reaction temperature (effect of H_2 addition) with Chubu Electric's SNR.

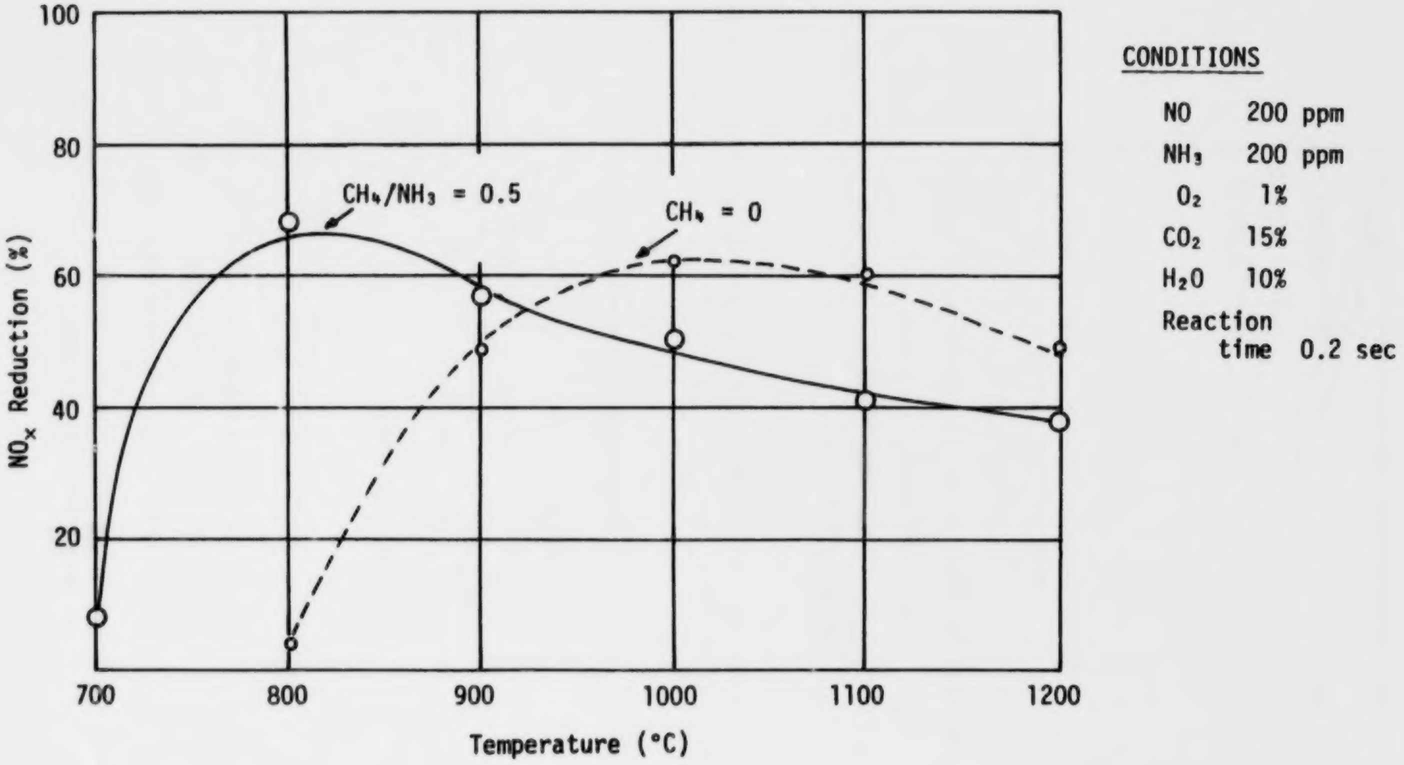
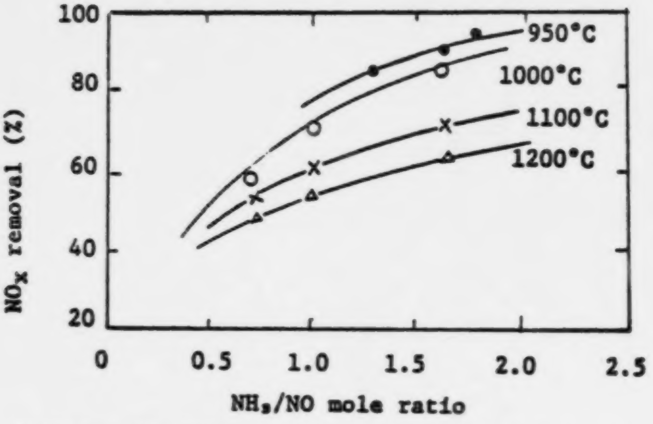


Figure 5-21. NO$_x$ reduction versus reaction temperature (effect of CH$_4$ addition) with Chubu Electric's SNR.



(Initial NO 200ppm, O_2 1%, CO_2 15%, H_2O 11%)

(Reaction time 0.2 sec.)

Figure 5-22. NH_3/NO mole ratio and NO_x removal with Chubu Electric's SNR.*

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* Initial NO, 200 ppm; O_2, 1 percent; CO_2, 15 percent; H_2O, 11 percent; reaction time, 0.2 second.

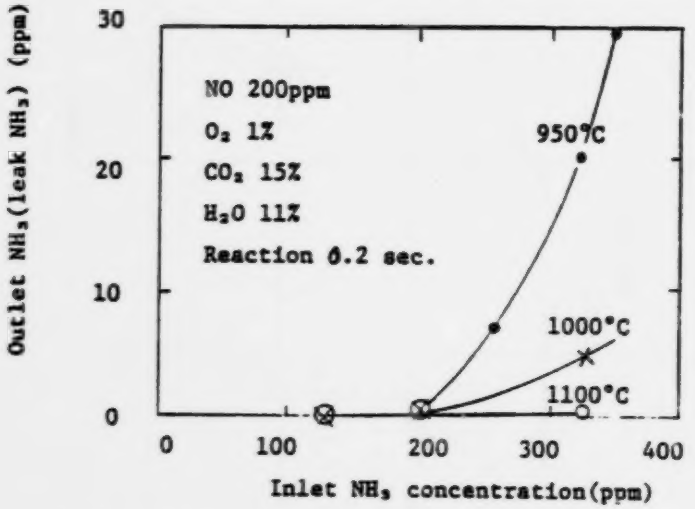

Figure 5-23. Inlet and outlet NH_3 at different temperatures with Chubu Electric's SNR.

5.4.3 Basic Study by MHI[5]

MHI has studied SNR jointly with Mitsubishi Chemical Industries (MCI), one of the largest chemical companies in Japan, and constructed a large-scale test plant for Chubu Electric at Chita Station. Figures 5-24 and 5-25 show some of the results of laboratory tests. To design the large plant, MHI assumed the 3 major reactions and determined the reaction rate constants of the three: k_1, k_2, and k_3.

$$4NO + 4NH_3 + O_2 \xrightarrow{k_1} 4N_2 + 6H_2O \qquad (5\text{-}9)$$

$$4NH_3 + 5O_2 \xrightarrow{k_2} 4NO + 6H_2O \qquad (5\text{-}10)$$

$$4NH_3 + 3O_2 \xrightarrow{k_3} 2N_2 + 6H_2O \qquad (5\text{-}11)$$

$$-\frac{d(NO)}{dt} = k_1(NO)^{\alpha}(NH_3)^{\beta}(O_2)^{\gamma_1} - k_2(NH_3)^{\delta}(O_2)^{\gamma_2} \qquad (5\text{-}12)$$

$$-\frac{d(NH_3)}{dt} = k_1(NO)^{\alpha}(NH_3)^{\beta}(O_2)^{\gamma_1} + (k_2 + k_3)(NH_3)^{\delta}(O_2)^{\gamma_3} \qquad (5\text{-}13)$$

The concentrations of NO and NH_3 during and after the reactions in a boiler can be calculated from equations 5-12 and 5-13. An example of the calculation, assuming the treatment of flue gas in a large scale utility boiler, is shown in Figure 5-26. The figure shows gas temperatures and NO_x removal efficiencies at distances within 1800 mm from the NH_3 injection point. The flue gas first passes an open space (0-400 mm) at about 1050°C in 0.04 second, and then passes the heat transfer zone (400-1800 mm) at 1050-920°C in 0.1 second. NH_3 is mixed with the flue gas in an open space and in a part of the heat transfer zone. Further mixing is accomplished in the dispersion reaction zone. NH_3 rapidly reacts with NO_x in the dispersion reaction zone.

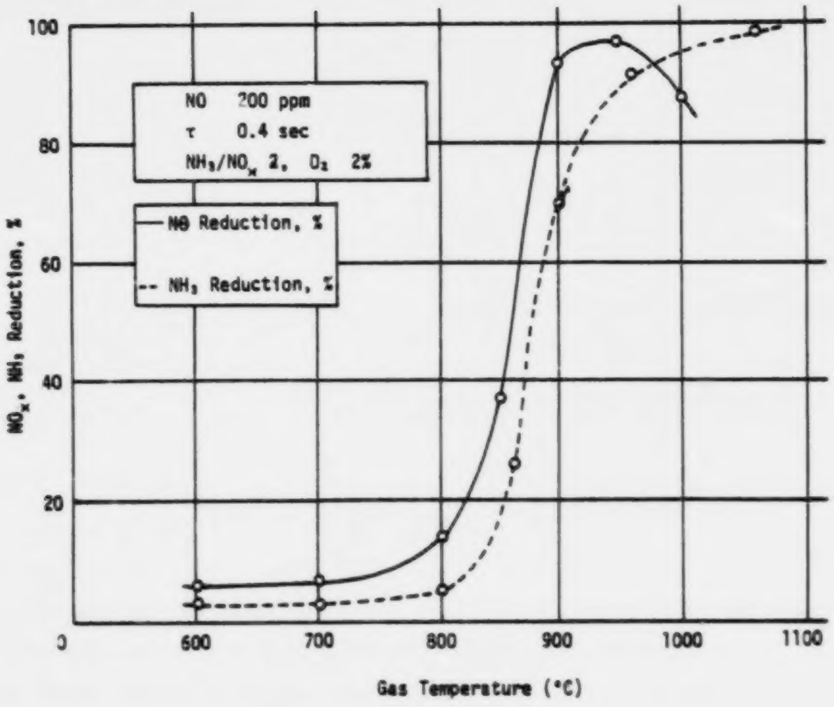

Figure 5-24. Laboratory data (effect of gas temperature) for the MHI-MCI joint study at Chita Station.

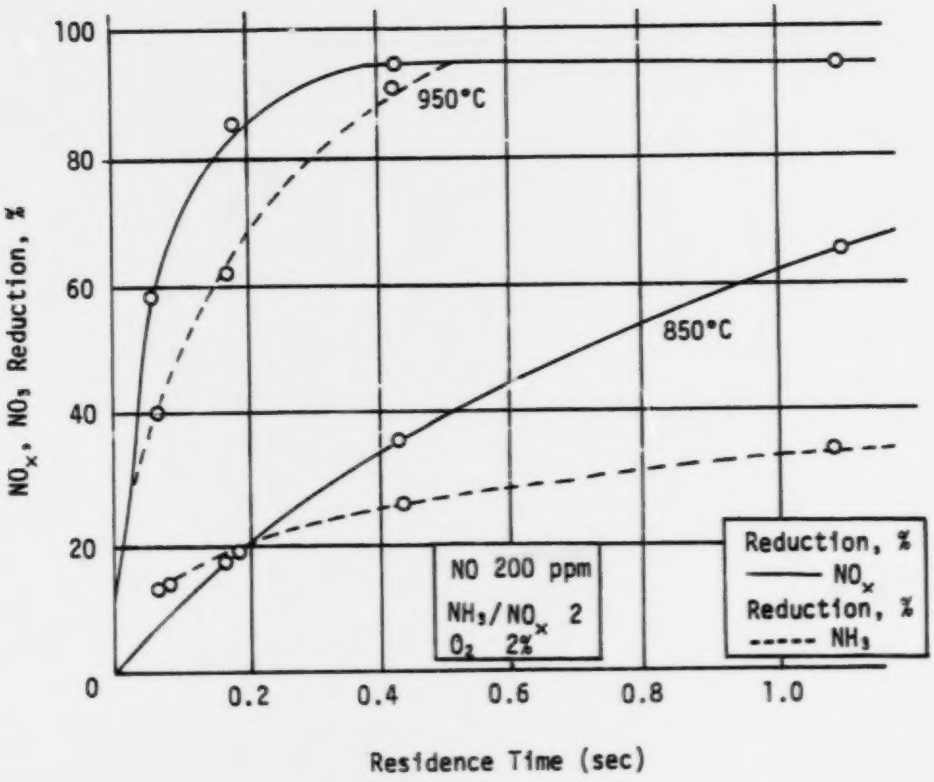

Figure 5-25. Laboratory data (effect of residence time) for the MHI-MCI joint study at Chita Station.

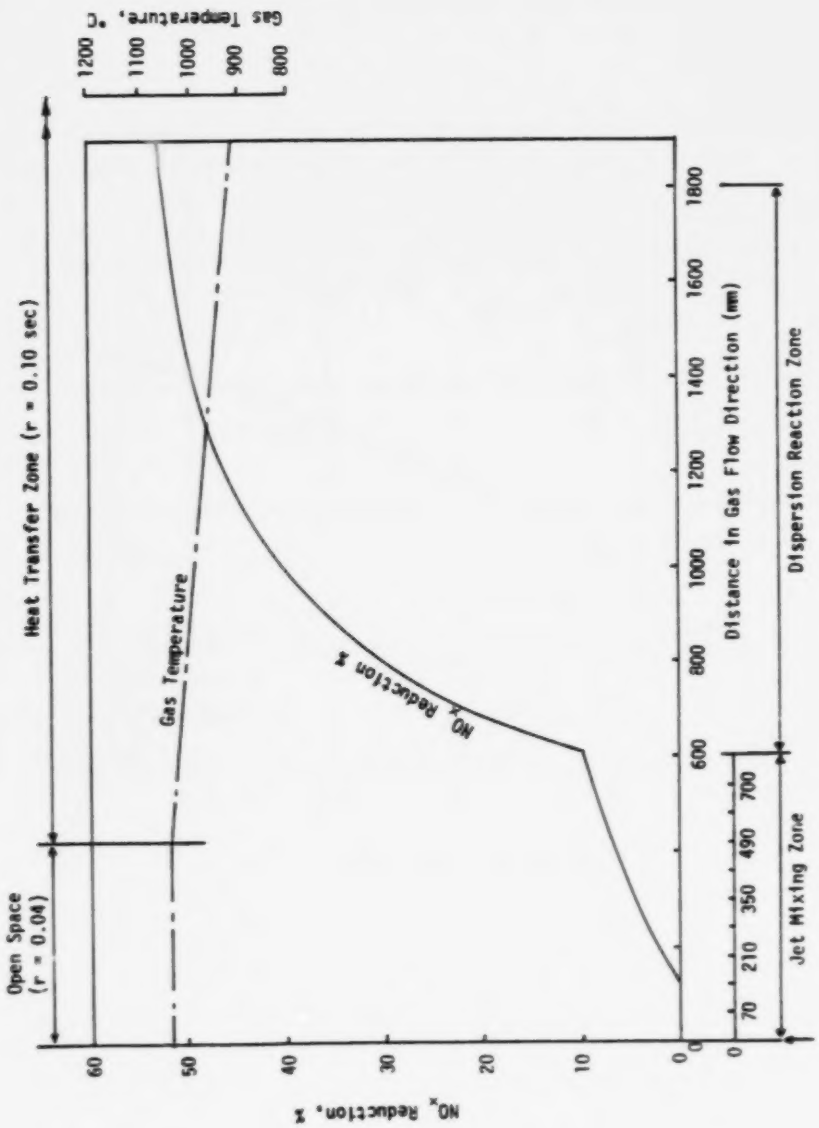

Figure 5-26. A calculation result by simulation on practical boiler.

5.4.4 Large Scale Plant Tests[4,5]

The large scale SNR tests have been performed on the No. 2 boiler at Chita Station which can generate 1225 tons/hr of steam and 375 MW of power. The total gas volume exceeds 1,000,000 Nm^3/hr. The boiler burns a low sulfur oil (0.2 percent S). The gas contains about 100 ppm SO_x, of which about 3 ppm is SO_3, and 110-140 ppm NO_x, virtually all of which is NO. The operation load of the boiler varies from 100 to 30 percent (375 to 113 MW). To cope with the temperature fluctuation due to the boiler load, 15 water-cooled ammonia injection nozzles were placed in two locations, front and rear, as shown in Figure 5-27. The structure of the nozzles is shown in Figure 5-28. The nozzle cooling systems are shown in Figures 5-29 and 5-30.

As shown in Figures 5-31 and 5-32 A, the gas temperature at 150-375 MW (40-100 percent load) ranges from 900 to 1150°C at the front nozzles and 800-1030°C at the rear ones. NH_3 is injected from the rear nozzles at 290-375 MW (78-100 percent load, 930-1030°C), from both nozzles at 225-290 MW (60-70 percent load), and only from the front nozzles below 60 percent load (below 1000°C). When the boiler load drops below 50 percent, no NH_3 is usually added because the amount of NO_x emission can be within the regulation.

Operation design conditions for 40 percent NO_x removal with less than 20 ppm of NH_3 leakage are shown by the shadowed lines in Figure 5-32 B, C, and D. A NH_3/NO_x mole ratio of 1.5 at full load and smaller ratios at lower load may be used.

Figure 5-33 compares the calculated NO_x removal efficiencies and NH_3 leakage with those observed in actual plant operation. The calculated efficiency and NH_3 leakage are shown by lines. The removal efficiency was a little lower when the initial NO_x concentration was 110 ppm than when it was 140 ppm. In both cases the predicted performance and the actual operating data agreed well for NO_x removal. Actual NH_3 leakage was a

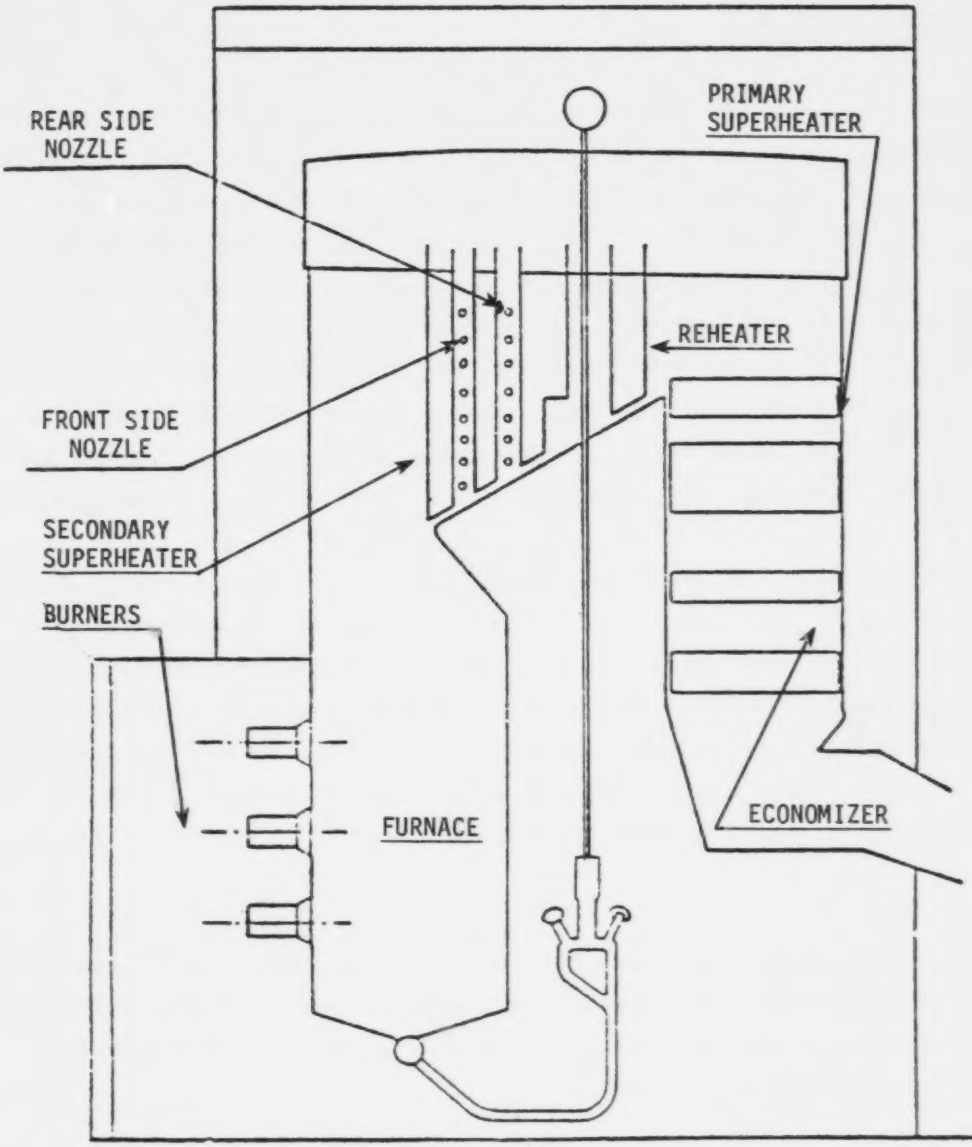
REAR SIDE NOZZLE
PRIMARY SUPERHEATER
REHEATER
FRONT SIDE NOZZLE
SECONDARY SUPERHEATER
BURNERS
FURNACE
ECONOMIZER

Figure 5-27. Locations of nozzles in the No. 2 Boiler at Chita Station.*

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* Boiler Type: Mitsubishi - CE Control, Radiant Reheat Divided.
Evaporation: 1225 T/H, 375 MW
Pressure: 176 atg.
Temperature: 571/540.6°C

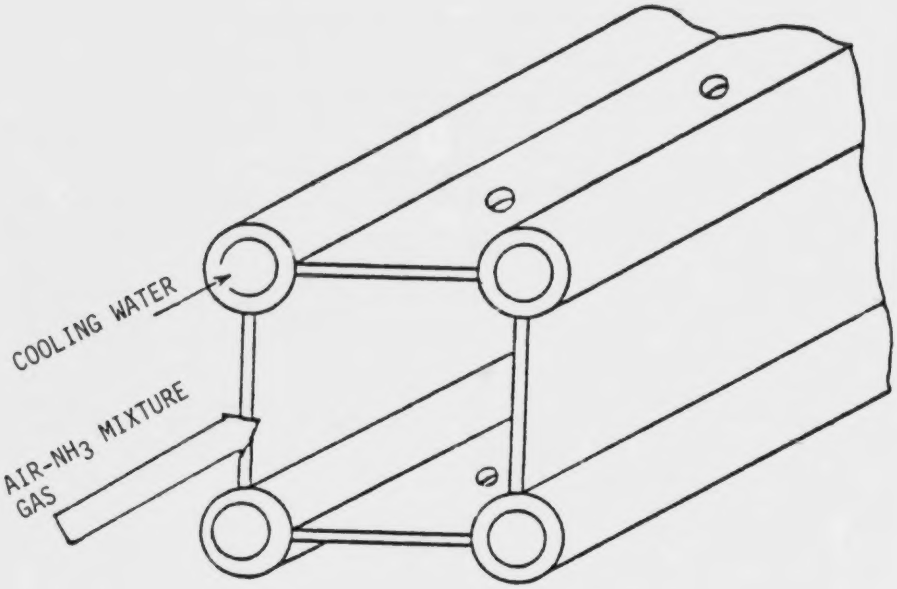
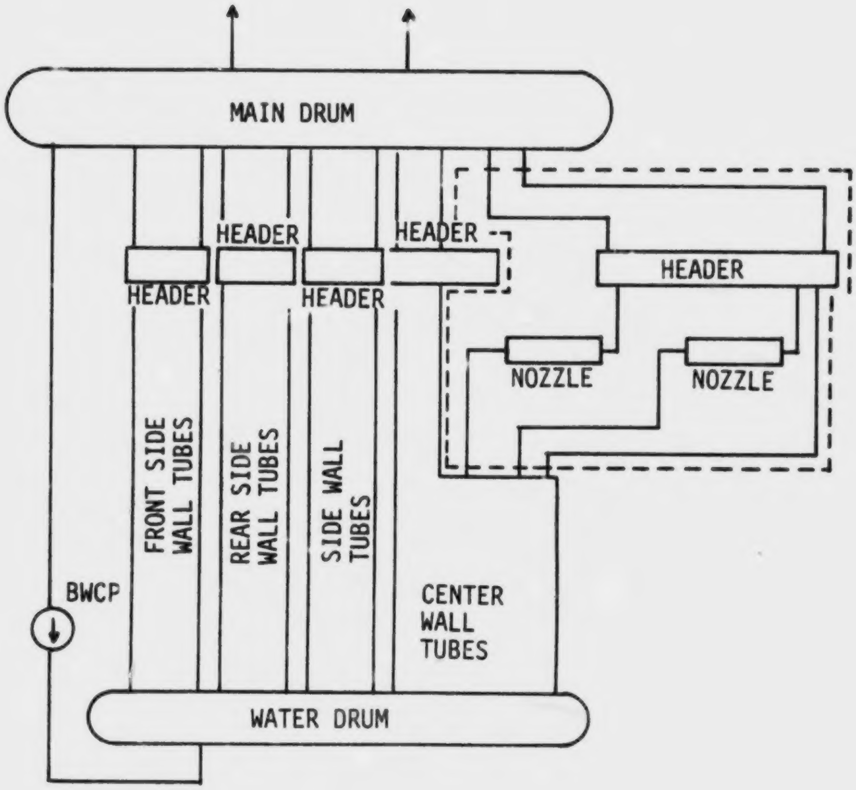

COOLING WATER
AIR-NH3 MIXTURE GAS

Figure 5-28. NH_3 injection nozzle in the No. 2 Boiler at Chita Station.



MAIN DRUM
HEADER
HEADER
HEADER
HEADER
HEADER
HEADER
NOZZLE
NOZZLE
FRONT SIDE WALL TUBES
REAR SIDE WALL TUBES
SIDE WALL TUBES
CENTER WALL TUBES
BWCP
WATER DRUM

Figure 5-29. Schematic flow of boiler water circulation for nozzle cooling in the No. 2 boiler at Chita Station.

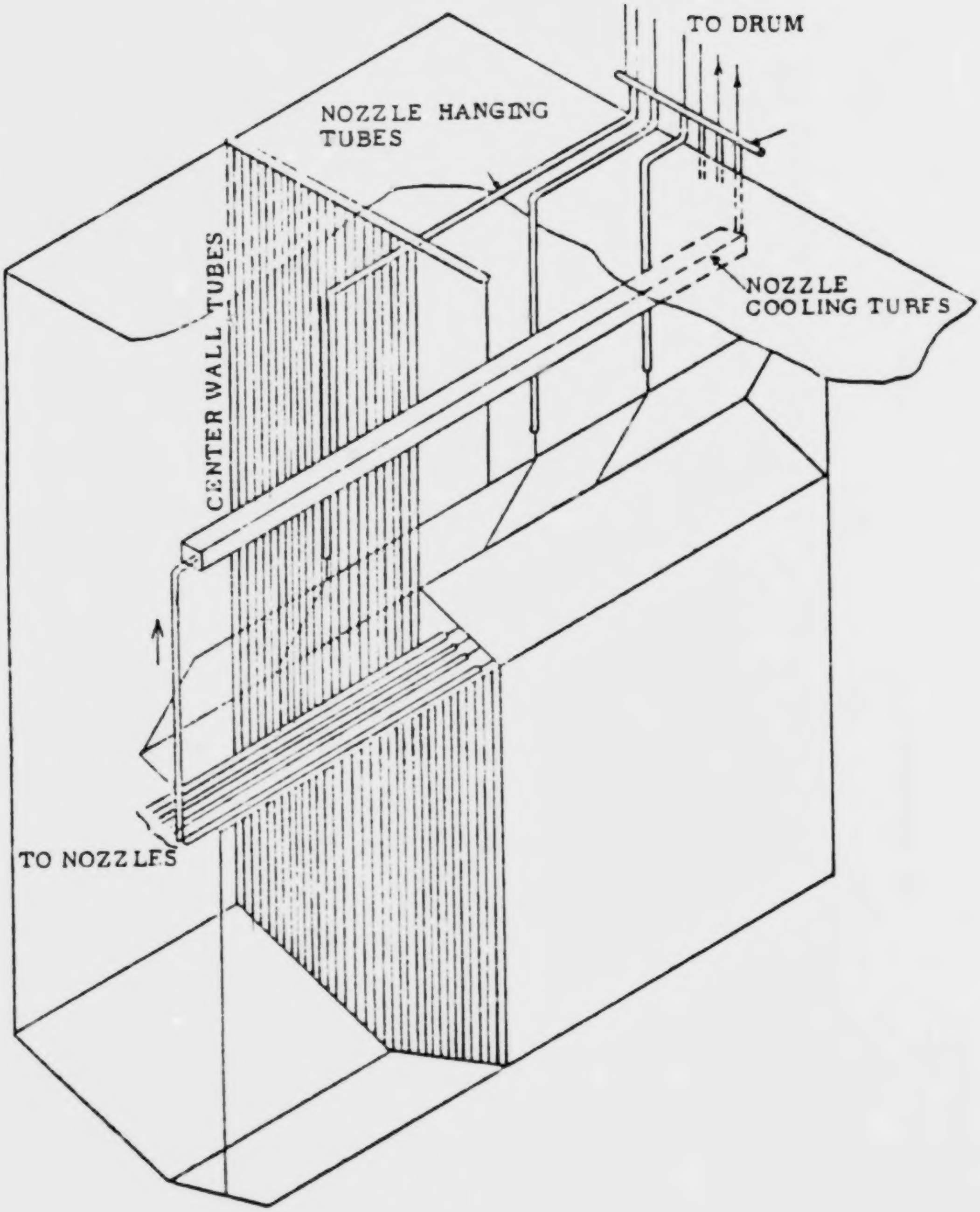

TO DRUM
NOZZLE HANGING TUBES
CENTER WALL TUBES
NOZZLE COOLING TUBES
TO NOZZLES

Figure 5-30. Concept of nozzle cooling systems on the No. 2 Boiler at Chita Station.

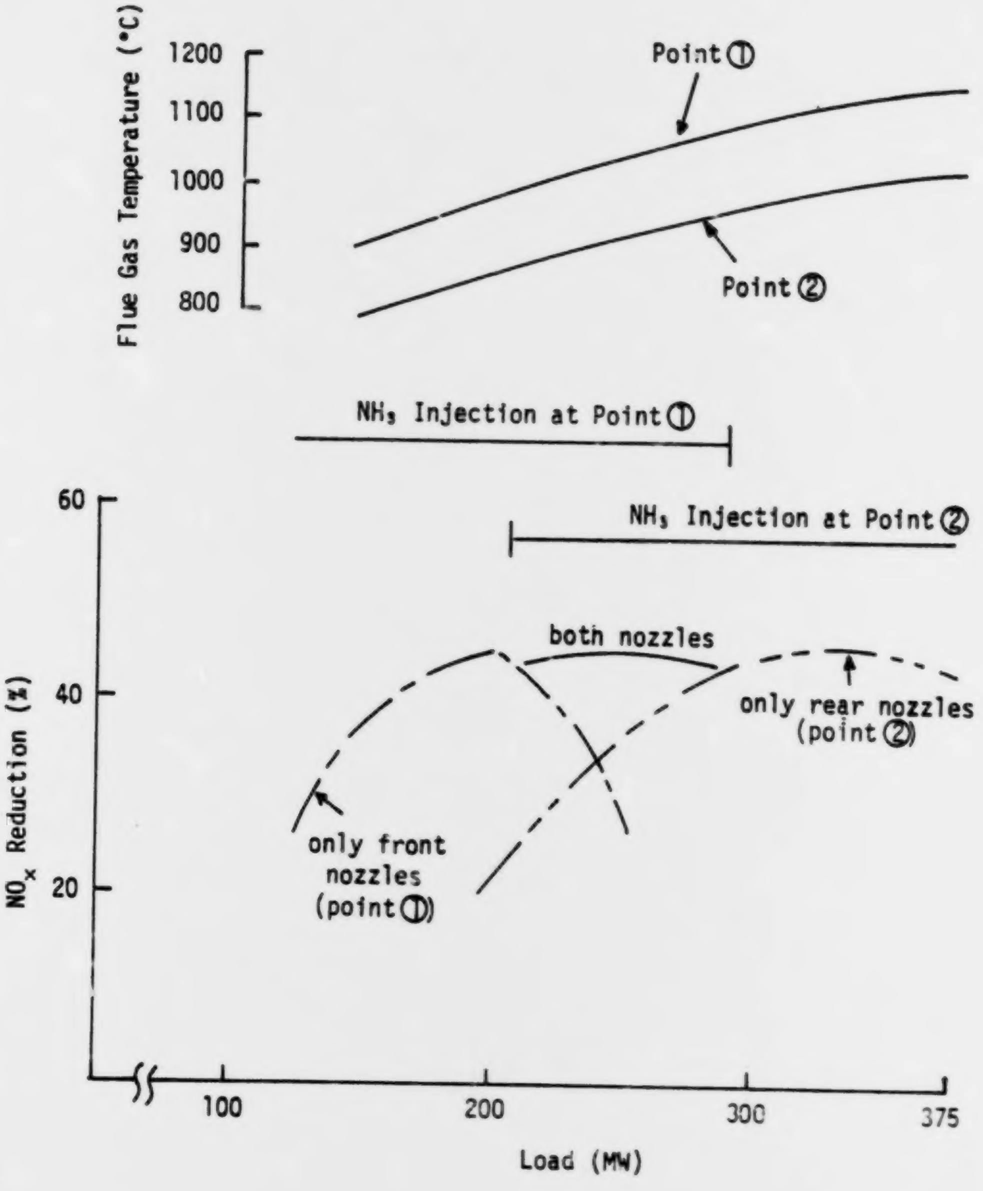


Figure 5-31. Effects of NH_3 injection position and load on NO_x reduction rates on the operation of the No. 2 boiler at Chita Station.

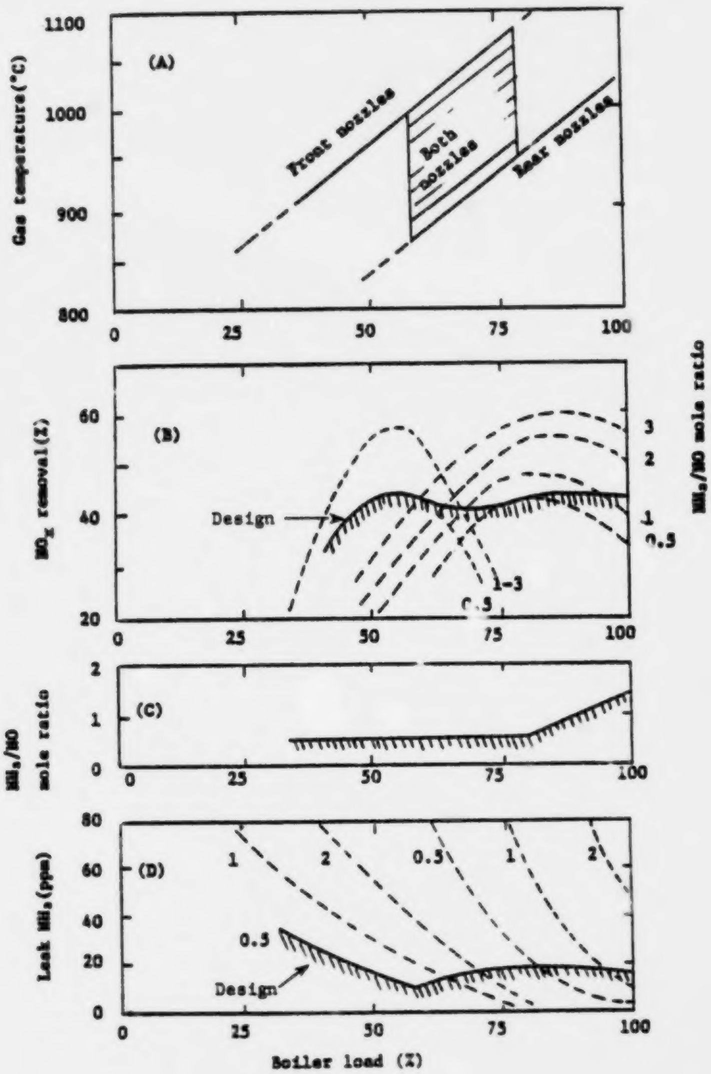


Figure 5-32. Data on the designed operation conditions and anticipated results at different operation loads of the No. 2 boiler at Chita Station (Mitsubishi Heavy Industries).

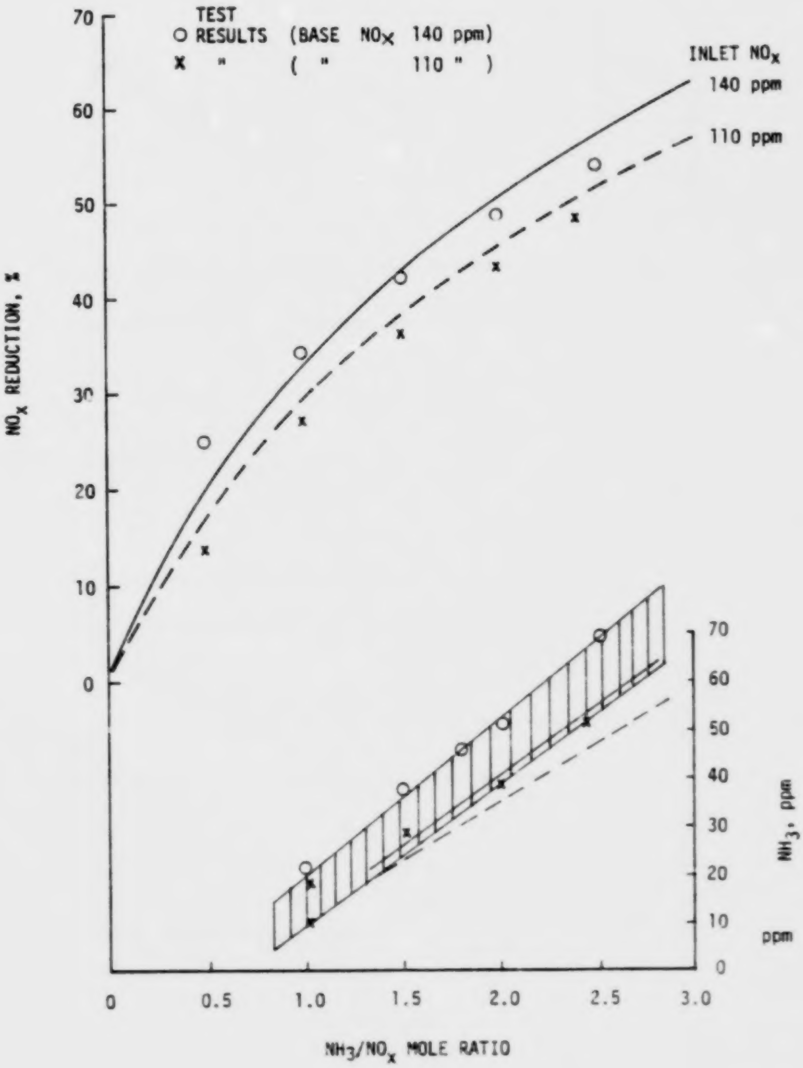


Figure 5-33. Comparison between test results and predicted performance of the No. 2 boiler at Chita Station.

little larger than the calculated amount. An NO_x removal efficiency of about 40 percent has been obtained with about 30 ppm of NH_3 leakage by using 1.5 mole of NH_3 for each mole of NO.

Operation was begun in February 1977 and has been virtually trouble-free except for deposits of ammonium salts with particulates in the air preheater. NO_x removal has been 40-45 percent. At the beginning of the operation a considerable amount of ammonium salt deposits formed. These increased the pressure drop and necessitated a water wash for their removal after 2 months' operation. The problem has been mitigated by increasing the soot blowing capacity. It is estimated that the water wash is required about twice a year. The stack usually gives no plume, but in winter a considerable plume was observed when outlet NH_3 exceeded about 40 ppm.

5.4.5 Economics of the Chita Plant

The SNR unit at the Chita plant cost 600 million yen ($3 million) in 1977 (1600 yen/kW, $8/kW). MHI has begun construction of an SCR plant for the existing No. 4 boiler of Chita Station which burns 0.2 percent sulfur oil. It will remove over 80 percent of the NO_x. The plant cost is estimated at about 3500 yen/kW ($17.50/kW). Therefore, the investment cost for SNR is a little less than half that for SCR. On the other hand, the NO_x removal efficiency of SNR is about half that of SCR while ammonia consumption and leakage are much higher. The water wash required for the air preheater increases the cost of SNR.

5.5 MITSUI PETROCHEMICAL, CHIBA PLANT

The SNR unit for the industrial boiler which can generate 120 tons/hr of steam (flue gas 120,000 Nm^3/hr, 40 MW equivalent) has been operated occasionally since 1976 at the Chiba plant, Mitsui Petrochemical. The plant has 5 boilers. One of the boilers was chosen for SNR because it has a relatively large volume per capacity and has enough space for ammonia injection nozzles. The space available is in the temperature range of about 700°C to 800°C, a little lower than the optimum reaction temperature (850-1000°C) for NO_x reduction by NH_3. Therefore, H_2 has been used with NH_3 to obtain optimum NO_x reduction at 700-800°C. Actually three nozzles have been placed in the temperature range and a total of 2 moles NH_3 and 8 moles H_2 has been injected for each mole of NO_x. Steam has been used for diluting the injection; air must be avoided because of the presence of H_2. Usually 35-40 percent of the NO_x is removed and there are 10-15 ppm of NH_3 leakage.

At the beginning of the operation, the boiler used 0.8 percent sulfur oil and leak NH_3 ranged from 20 to 30 ppm to achieve about 45 percent NO_x removal. The air preheater became plugged within a few weeks by the ammonium bisulfate deposit. Since then, sulfur-free fuel, either gas or oil (S = 0. 02 percent or below), has been used for the boiler. Operation has been trouble-free.

Mitsui Petrochemical recently installed an SCR unit for a larger boiler (200,000 Nm^3/hr) which burns low sulfur oil (S = 0.2-0.6 percent) to reduce more than 90 percent of the NO_x with NH_3 leakage below 5 ppm. The air preheater has no dust plugging problem because of the low NH_3 leakage. Mitsui Petrochemical estimates that the overall cost to remove an equal amount of NO_x is lower with SCR than with SNR.

5.6 OTHER SNR PLANTS

As shown in Table 5-1, there are five relatively large SNR units constructed in 1976 - later. Those are all for oil or petrochemical companies and have been used for emergency when a photochemical smog warning is issued or when the total NO_x emission from the refinery or the petrochemical plant exceeds the regulation. Those units can be operated continuously if needed and are capable of removing 45-57 percent of NO_x by adding 1-2 moles of NH_3 together with H_2 to 1 mole of NC_x.

5.7 COMPARISON OF SCR, SNR AND THE COMBINED PROCESS

Table 5-2 shows estimated NO_x removal efficiency and ammonia leakage when flue gas containing 200 ppm NO_x is treated by SCR, SNR and the combined process.

It is possible to attain 95 percent NO_x removal efficiency by SCR when sufficient amounts of NH_3 and catalyst are used (No. 1 of Table 5-2). However, optimum operation may be represented by Nos. 3 and 5 which attain 80-85 percent NO_x removal with 5 ppm of NH_3 leakage using a smaller amount of NH_3 and catalyst, because the investment cost as well as consumption of power and ammonia is low and ammonium bisulfate problem is reduced. When lower removal efficiency is adequate, both catalyst and NH_3 may be further reduced. If increasingly stringent regulations are expected, the reactor vessel and the fan with sufficient capacities may be installed and the amounts of catalyst and NH_3 may be increased to meet the regulations.

SNR with 1-1.5 moles NH_3 for 1 mole NO_x (200 ppm in flue gas) may give 40-50 percent removal efficiency with 30-40 ppm NH_3 leakage. Use of 2-3 moles of NH_3 may give 55-60 percent efficiency with 50-80 ppm of NH_3 leakage which may be unacceptably high. Placing a small amount of parallel flow type SCR catalyst in a boiler duct at 300-400°C will reduce NH_3 leakage and increase NO_x removal efficiency (Nos. 22, 23, 32, 34, and 42). By using about 30 parts or less catalyst, the increase in the pressure drop may be below 30 mm H_2O and may not require increasing the capacity of the fan. The combination of SNR and SCR with the small amount of catalyst may be useful for existing boilers which have no space to install an SCR reactor or an additional fan. The NO_x removal efficiency may be further increased by adding a small amount of NH_3 before the catalyst bed (Nos. 23, 24, 34, 35 and 44). This method, however, may complicate the process control.

It is possible by the combined system to attain 80 percent or more NO_x removal with 10 ppm of NH_3 leakage when more than 50 parts of the

TABLE 5-2. COMPARISON OF SCR, SNR AND COMBINED SYSTEMS FOR AN INLET NO_x CONCENTRATION OF 200 PPM

No.	NH_3 to Boiler (ppm)	Boiler Outlet (ppm)		NH_3 to Reactor (ppm)	Catalyst (Relative Amount)	Reactor Outlet (ppm)		NO_x Removal (%)
		NO_x	NH_3			NO_x	NH_3	
1	0	200	0	210	100	10	10	95
2	0	200	0	190	100	20	5	90
3	0	200	0	180	90	30	5	85
4	0	200	0	195	80	20	10	90
5	0	200	0	170	80	40	5	80
6	0	200	0	185	70	30	10	85
7	0	200	0	160	70	50	5	75
8	0	200	0	175	60	40	10	80
9	0	200	0	140	60	70	5	65
10	0	200	0	180	50	40	15	80
11	0	200	0	155	50	60	10	70
12	0	200	0	135	40	80	10	60
21	200	120	30	0	0	120	30	40
22	200	120	30	0	20	100	10	50
23	200	120	30	50	30	60	15	70
24	200	120	30	50	50	50	10	75
31	300	100	40	0	0	100	40	50
32	300	100	40	0	30	70	10	65
33	300	100	40	0	50	60	5	70
34	300	100	40	30	30	50	15	75
35	300	100	40	35	50	40	10	80
41	400	90	50	0	0	90	50	55
42	400	90	50	0	20	60	20	70
43	400	90	50	0	40	50	10	75
44	400	90	50	20	50	30	10	85
51	600	80	80	0	0	80	80	60
52	600	80	80	0	20	30	30	80
53	600	80	80	0	40	20	20	90
54	600	80	80	0	70	10	10	95

catalyst are used (Nos. 35, 44, and 54). However, NH_3 consumption is high and the catalyst may cause too great a pressure drop to be used in the boiler duct without increasing the fan capacity. If a separate reactor or an additional fan is needed, SCR only may be preferred to the combined system.

5.8 EVALUATION

SNR is the simplest method for removing NO_x from flue gas and is useful for NO_x removal up to about 50 percent. It has, however, the following disadvantages:

1) For many existing boilers, space for ammonia injection is not available in a suitable temperature range.

2) SNR has a limited NO_x removal efficiency particularly for large boilers due to the difficulty of rapid uniform gas mixing and the limited reaction time in the suitable temperature range.

3) Both consumption and NH_3 leakage are high.

The practical NO_x removal efficiency for utility boilers may be about 40 percent when 20 ppm of NH_3 leakage is allowed and 30 percent when NH_3 leakage is kept at about 10 ppm. With flue gas containing a considerable amount of SO_x, the problem of fouling the air preheater with ammonium bisulfate may be serious when NH_3 leakage is high.

To obtain 50-70 percent NO_x removal efficiency with 10 ppm of NH_3 leakage, a small amount of catalyst should be used at 300-400°C. The combination system may be useful for boilers which have no room for a separate SCR reactor and have a small excess fan capacity (below about 30 mmH_2O).

SNR may give a better than average NO_x removal efficiency for some furnaces in which flue gas has a relatively large retention time at 850-1000°C.

Because of the low investment cost, SNR may be particularly suitable for 40-50 percent NO_x reduction for emergency, as has been needed in some districts in Japan.

5.9 REFERENCES

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2. Kasaoka, S., Kagakukojo, 20-7, 1975 and Nenryokyokaishi, 56-3, 1977. In Japanese.

3. Sato, M., *et al.* CRIEPI report No. 27626, 1977. In Japanese.

4. Operating Experiences of High-Temperature Noncatalytic De-NO_x Process at No. 2 Unit of Chita Thermal Power Station. Central Technical Research Lab., Chubu Electric. Report for IERE, 1978. In English.

5. Noncatalytic NO_x Reduction Process Applied to Large Utility Boiler. MHI Report. November 1977. In English.

SECTION 6

OTHER DRY PROCESSES

6.1 INTRODUCTION

The following three dry simultaneous SO_x and NO_x removal processes have been developed:

1) Activated carbon process in which ammonia reduces NO_x to N_2,

2) Copper oxide process in which ammonia reduces NO_x to N_2,

3) Electron beam radiation process in which ammonia is used to produce ammonium sulfate and nitrate.

With processes 1) and 2), SO_x is absorbed by either activated carbon containing a metal catalyst or copper oxide supported by an alumina carrier. Sulfuric acid or sulfate is formed, while NO_x is reduced to N_2 by ammonia. In both processes, concentrated SO_2 is recovered by heating the carbon or by reducing copper sulfate with hydrogen.

With process 3), flue gas is mixed with ammonia and exposed to an electron beam. Powdery ammonium sulfate and nitrate are obtained as by-products.

The reaction temperature is 220-250°C for 1), 350-400°C for 2, and about 100°C for 3). The advantage of these processes is that they remove

SO_x and NO_x simultaneously in a dry state and require no reheating of the treated gas. On the other hand, process 1) requires a large amount of carbon, while 2) requires hydrogen for regeneration and 3) requires a high-intensity electron beam.

Processes 1 and 3 have been tested in pilot plants which can treat 1000-5000 Nm^3/hr. Process 2 has been applied commercially to the flue gas (120,000 Nm^3/hr) from an industrial boiler. All three processes can remove 80-90 percent of SO_x and NO_x.

SO_x and NO_x can also be removed by a combined system of SCR and FGD. The combination of wet FGD followed by SCR is expensive; it requires a large amount of energy for heating the gas after FGD. Recent improvements of SCR catalysts have made it possible to use SCR first on dirty gas without cleaning, and then use FGD. The combination seems less expensive although there is no large commercial plant yet using it. Operation of large plants with this combination system and the dry simultaneous removal process will determine which of the two is better.

Catalytic decomposition of NO_x to N_2 and O_2 has been studied by a few companies but so far does not seem practical because of the low decomposition ratio and the short life of catalysts.

As a dry process for NO_x removal, the molecular sieve adsorption-desorption process has been used for treating the tail gas from a nitric acid plant of Nissan Chemical.

6.2 REACTION OF ACTIVATED CARBON WITH NO_x

6.2.1 Introduction

Activated carbon has the following functions useful for removing NO_x:

1) Adsorption and desorption - It adsorbs NO_2 below 100°C and desorbs it above 100°C.

2) Oxidation - It promotes the oxidation of NO to NO_2 below 100°C.

3) Catalytic reduction - Above 100°C, it promotes the following reactions:

$$6NO + 4NH_3 \longrightarrow 5N_2 + 6H_2O \tag{6-1}$$

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \tag{6-2}$$

$$6NO_2 + 8NH_3 \longrightarrow 7N_2 + 12H_2O \tag{6-3}$$

$$2NO + 2CO \longrightarrow N_2 + 2CO_2 \tag{6-4}$$

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O \tag{6-5}$$

$$2NO + C \longrightarrow N_2 + CO_2 \tag{6-6}$$

$$NO_2 + 2CO \longrightarrow \tfrac{1}{2} N_2 + 2CO_2 \tag{6-7}$$

The NO_2 adsorbing capacity is not large enough to treat a large amount of gas, as will be explained below. Carbon has been used in several small wet-process NO_x removal plants as the catalyst for oxidation of NO to NO_2. The use is also limited to small amounts of gas at low temperatures.

For treating a large amount of flue gas above 100°C, carbon is useful as an NO_x reduction catalyst. Addition of metal compounds increases the activity. Although the efficiency is less than that of SCR catalysts (Chapters 3 and 4), carbon can remove SO_x simultaneously.

6.2.2 NO_x Adsorption and Desorption[1]

Table 6-1 shows the NO_x adsorption capacity of activated carbon under different conditions. NO_2 is adsorbed by carbon fairly quickly but NO is not. NO, however, is oxidized to NO_2 in the presence of O_2 by the catalytic reaction of carbon and the resulting NO_2 is adsorbed. The adsorption capacity is fairly large at low temperature and humidity. Since flue gases from boilers and furnaces have higher temperatures and humidities, the carbon may not be useful as an NO_x adsorbing agent for those gases.

TABLE 6-1. NO_x ADSORPTION CAPACITY OF ACTIVATED CARBON
(mg NO_x/g activated carbon)

Relative Humidity, percent	Adsorption Temperature		
	30°C	50°C	70°C
14	120.0		56.8
20		110.2	
35	104.0	95.0	
40			36.8
60		75.4	
75	67.7		

NO_x adsorbed by carbon is desorbed either by washing with water or by heating. Water-washing produces a dilute nitric acid. Higher temperatures are more favorable for the washing, as shown in Figure 6-1. The wet carbon has a poor NO_x adsorption ability and should be dried before reuse for adsorption. However, wet carbon is effective for SO_x adsorption.

Figure 6-2 shows the desorption rates when carbon is heated in a nitrogen gas stream at different temperatures. Above 150°C, desorption occurs fairly rapidly, but carbon is consumed in reaction 6-8 to form NO

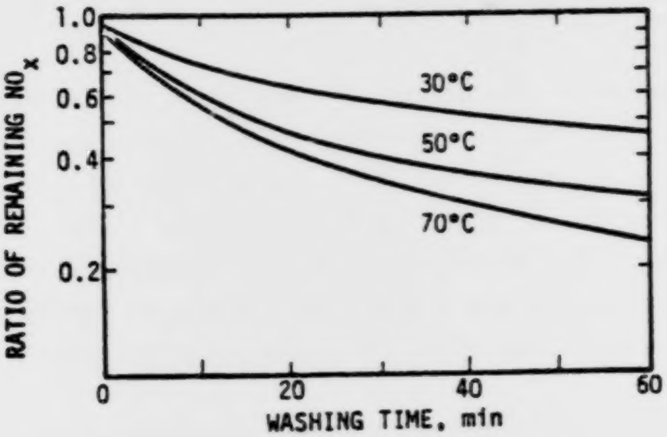

Figure 6-1. Desorption of NO_x adsorbed by activated carbon (6 mm in diameter) by washing with water at different temperatures.

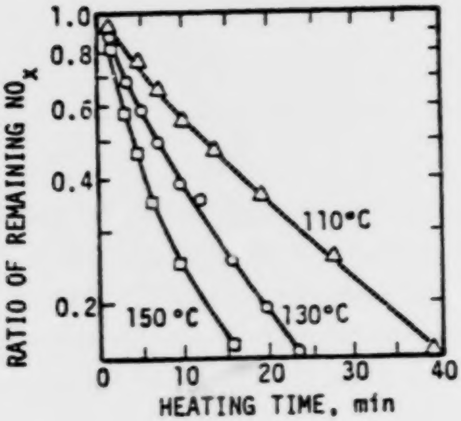

Figure 6-2. Desorption of NO_x adsorbed by activated carbon by heating at different temperatures.

and CO_2. When the gas is heated above 450°C, a larger amount of carbon is consumed by reaction 6-9 to form N_2 and CO_2.

$$2NO_2 + C \longrightarrow 2NO + CO_2 \qquad (6\text{-}8)$$

$$2NO_2 + 2C \longrightarrow N_2 + 2CO_2 \qquad (6\text{-}9)$$

Heating the carbon in a stream of reducing gas lowers the carbon consumption substantially and increases the conversion of NO_x to N_2 (Table 6-2).[1]

TABLE 6-2. DESORPTION OF NO_x IN REDUCING GAS

Gas	Temperature, °C	Conversion Ratio of Adsorbed NO_x into N_2 on Desorption, percent
H_2	200	10
	400	68
	600	100
CO	200	12
	400	70
	600	100
NH_3	200	100
	400	100
	600	100
He (Inert Gas)	200	0
	400	5
	600	70

6.2.3 Catalysts for Ammonia Reduction

Among the reducing gases mentioned previously, ammonia is the most useful for flue gas treatment. Unlike other reducing gases, ammonia reacts with NO_x selectively and is consumed only slightly by O_2 in the flue gas. The effect of carbon on the reaction between NO_x and NH_3 is further increased by adding a small amount of base metal compounds (Table 6-3).[1] Copper and vanadium have been found most effective. Takeda Chemical has commercially produced activated carbon catalysts with metallic components.

TABLE 6-3. EFFECT OF ADDITION OF BASE METAL COMPOUNDS TO CARBON ON NO_x REDUCTION EFFICIENCY (NO, 2000 ppm; NH_3, 3000 ppm; SV, 3000 hr^{-1})

	NO_x Reduction Efficiency, percent		
Metal	110°C	150°C	250°C
None	38	44	78
Ti		65	
Cr	55	70	95
Mn	50	67	88
Fe	52	67	90
Co	63	75	98
Ni		67	
Cu	91	99	100
V	80	88	100
Mo		70	
W		65	

The efficiency shown in Table 6-3 is obtained at an SV of 3000 hr^{-1}. An SV of about 1000 hr^{-1} has been used commercially, considerably less than the 5000-10,000 used in SCR (Chapters 3 and 4). It is possible to increase the reactivity of carbon by adding larger amounts of metal components.

However, because of local overheating from the heat of reaction, this addition can result in the combustion of carbon.

Hitachi Ltd. has found that activated carbon treated with ammonium bromide is effective even at 100°C for NO_x reduction by ammonia.[2] The low-temperature activity is useful for energy savings, but at the low temperature ammonium sulfate and bisulfate will deposit on the carbon.

6.2.4 Simultaneous Removal of SO_x and NO_x

Activated carbon has been used commercially as an adsorbent for SO_2. As shown in Figure 6-3, a lower temperature is suitable for SO_2 adsorption while a higher temperature favors NO_x removal by selective catalytic reduction. The optimum temperature for simultaneous removal of SO_x and NO_x is 220-230°C. NO_x is converted to N_2 while SO_2 is adsorbed by the carbon to form H_2SO_4 and NH_4HSO_4. The ratio of NH_4HSO_4 to H_2SO_4 increases as the temperature decreases. $(NH_4)_2SO_4$ also forms at lower temperatures.

$$SO_2 + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow H_2SO_4 \qquad (6\text{-}10)$$

$$H_2SO_4 + NH_3 \longrightarrow NH_4HSO_4 \qquad (6\text{-}11)$$

$$H_2SO_4 + 2NH_3 \longrightarrow (NH_4)_2SO_4 \qquad (6\text{-}12)$$

The formation of NH_4HSO_4 and $(NH_4)_2SO_4$ not only increases ammonia consumption but also lowers catalyst activity.

The H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$ contained in the carbon can be removed by water-washing resulting in a dilute solution of the compounds. Although the solution can be used for fertilizer production, a large amount of energy is required to concentrate it.

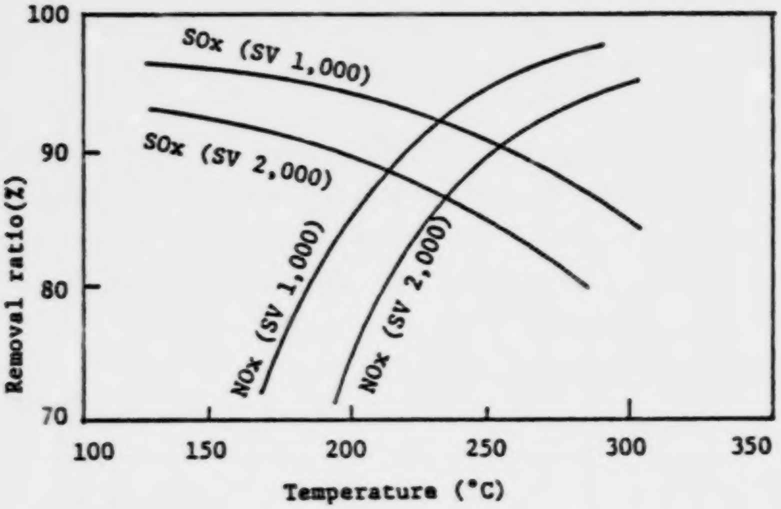

Figure 6-3. Removal efficiencies of activated carbon.

Thermal regeneration has been applied to the processes tested in pilot plants. The carbon, which contains sulfuric acid and the sulfates, is heated at about 350°C in an inert gas to remove those compounds by the following reactions:

$$H_2SO_4 + C \longrightarrow SO_2 + CO + H_2O \qquad (6\text{-}13)$$

$$2H_2SO_4 + C \longrightarrow 2SO_2 + CO_2 + 2H_2O \qquad (6\text{-}14)$$

$$2NH_4HSO_4 + C \longrightarrow 2NH_3 + 2H_2O + 2SO_2 + CO_2 \qquad (6\text{-}15)$$

$$3NH_4HSO_4 \longrightarrow NH_3 + 6H_2O + 3SO_2 + N_2 \qquad (6\text{-}16)$$

By thermal regeneration, a concentrated SO_2 gas is recovered which can be used for sulfuric acid or elemental sulfur production. However, a considerable amount of carbon is lost due to reactions 6-13, 6-14 and 6-15.

The activated carbon used in Japan for SO_x and NO_x removal is of high quality and free from the burning problem. Low cost carbon usually contains a considerable amount of ash containing alkali and alkali earth elements which promote burning. To produce high quality carbon, the ash components are reduced to less than 1 percent. However, it costs nearly 2 million yen/ton ($10,000/ton) while the carbon for SO_2 removal costs 800,000 yen/ton ($4000/ton). About 1000 tons of carbon are required for treating flue gas from a 300 MW boiler. The cost of carbon for simultaneous removal is estimated to be lowered to 1,250,000 yen/ton ($6250/ton) by mass production if demand is sufficient. Further cost reduction is desired before the process can be applied commercially.

6.3 SUMITOMO HEAVY INDUSTRIES CARBON PROCESS FOR SIMULTANEOUS REMOVAL

6.3.1 Introduction

In 1971, Sumitomo Heavy Industries (SHI, formerly Sumitomo Shipbuilding), one of the largest shipbuilding and plant constructing companies, constructed a prototype FGD plant which could treat 175,000 Nm^3/hr of flue gas from an oil-fired boiler at Sakaiko Station, Kansai Electric. The plant used an activated carbon process with moving beds and thermal regeneration. The plant was operated well for about 4 years but the operation was given up because of the high cost of carbon consumption.

Using the moving bed technology, SHI has developed a simultaneous SO_x and NO_x removal process and constructed a pilot plant which can treat 2000 Nm^3/hr of the flue gas from an iron-ore sintering machine at the Wakayama Works, Sumitomo Metal. The plant was constructed with funds of the Japan Steel Federation and was operated in 1976. SHI also constructed and operated a smaller pilot plant (500 Nm^3/hr) for the selective catalytic reduction of a gas from an iron-ore sintering machine. This plant had a similar moving bed.

6.3.2 Operation of the 2000 Nm^3/hr Pilot Plant[3]

After passing through an electrostatic precipitator, the flue gas from the sintering machine of the 2000 Nm^3/hr pilot plant contains 150-200 ppm NO_x, 150-250 ppm SO_2, 12-15 percent O_2, and 80-150 mg/Nm^3 of particulates at about 150°C. In some of the tests, SO_2 was added to the gas to increase the concentration to 350-480 ppm.

A flowsheet of the pilot plant is shown in Figure 6-4. The carbon is cylindrical with a diameter of 4 mm, a height of 6 mm, and a crushing strength of 10 kg/granule. The gas is heated to 200-230°C by an oil-fired furnace, ammonia is injected and introduced in a moving bed reactor. The carbon catalyst moves slowly downward in the reactor while the gas is passed through the carbon bed in a cross flow. About 90 percent of the SO_2, 85 percent of the NO_x, and 75 percent of the particulates were removed with an NH_3 leakage of 5 ppm and a pressure drop of 200 mmH_2O under the standard conditions shown below.

Reaction Temperature	220°C
SV	1000 hr^{-1}
NH_3	370 ppm

The carbon leaving the moving bed reactor contains H_2SO_4 and NH_4HSO_4 as was described in Section 6.2.4 (reactions 6-10 - 6-12). The carbon is discharged from the reactor, screened to remove dust, and sent to a regenerator which is also a moving bed reactor. The carbon again moves slowly downwards while a hot inert gas at 350°C is passed through the carbon bed in a parallel flow to decompose the H_2SO_4 and NH_4HSO_4 and to purge concentrated SO_2 by reactions 6-13 - 6-16 presented in Section 6.2.4. The inert gas is produced by incomplete combustion of propane and contains 1-1.5 percent CO, 9.5-10 percent CO_2, about 0.8 percent H_2, and 0.5 percent O_2. The purged concentrated SO_2 can be used to produce sulfuric acid or elemental sulfur. The regenerated carbon is returned to the first reactor.

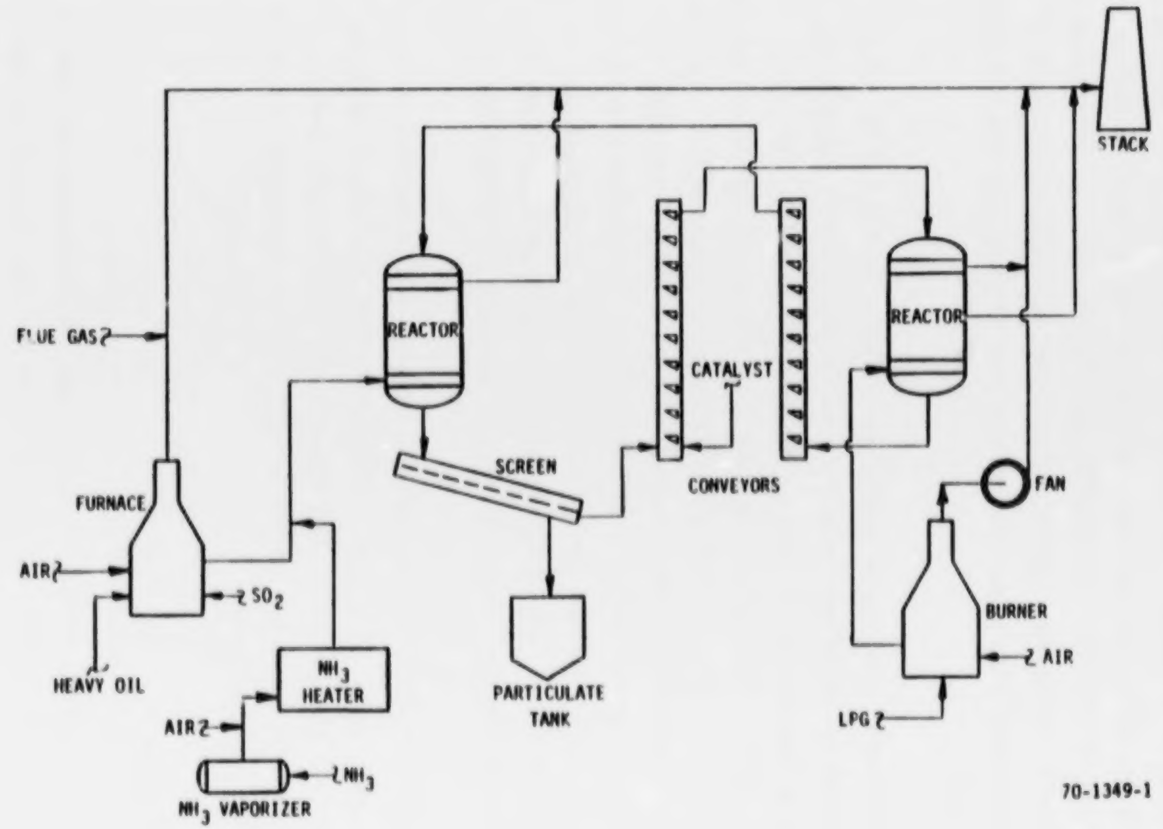
FLUE GAS
FURNACE
AIR
HEAVY OIL
SO_2
REACTOR
SCREEN
NH_3 HEATER
AIR
NH_3
NH_3 VAPORIZER
PARTICULATE TANK
CATALYST
CONVEYORS
REACTOR
FAN
BURNER
AIR
LPG
STACK
70-1349-1

Figure 6-4. Flowsheet of a 2000 Nm^3/hr pilot plant using the SHI carbon process for simultaneous removal of SO_x and NO_x.

The result of a 2300-hour continuous test is shown in Figure 6-5. The test was carried out under the above-mentioned standard conditions except for the temperature fluctuation. At 210-230°C, 90-97 percent of the SO_2 and 85-90 percent of the NO_x were removed. At the beginning and the end of the test, the temperature was low (180-190°C) and the NO_x removal efficiency was low (40-50 percent), while SO_2 removal efficiency was maintained above 95 percent. Pressure drop of the gas was maintained between 180 and 210 mmH_2O throughout the test.

Tests at different conditions are shown in Figures 6-6 - 6-9. The reactor temperature of 220°C was required for 85 percent NO_x removal and 230°C was required for nearly 90 percent removal at an SV of 1000 hr^{-1} (Figures 6-6 and 6-7). Increasing the amount of ammonia raised not only NO_x removal efficiency but also SO_2 removal efficiency because much of the SO_2 is removed by the formation of NH_4HSO_4 and ammonia leakage increased (Figure 6-8). On the other hand, an increase in the SO_2 concentration at a fixed NH_3 concentration resulted in a slight decrease in the removal efficiencies (Figure 6-9). The standard NH_3 concentration (370 ppm) is approximately 1 mole NH_3 to 1 mole NO_x plus 1 mole NH_3 to 1 mole SO_2.

Based on the 2300 hours of operation, the carbon consumption is estimated to be 113 percent for a year (3320 hours of operation) with an SO_2 concentration of 150-250 ppm. The NO_x and SO_x removal efficiencies were maintained by replacing the carbon at this rate. The plant operation has been virtually trouble-free.

6.3.3 Cost Estimation

Based on the operation of pilot plants, SHI has estimated the cost for the simultaneous removal of SO_x and NO_x and also for NO_x removal by SCR with a ferrite catalyst. These estimates are for flue gas from a 500 MW coal-fired boiler containing 500 ppm SO_2 and 600 ppm NO_x (Table 6-4).

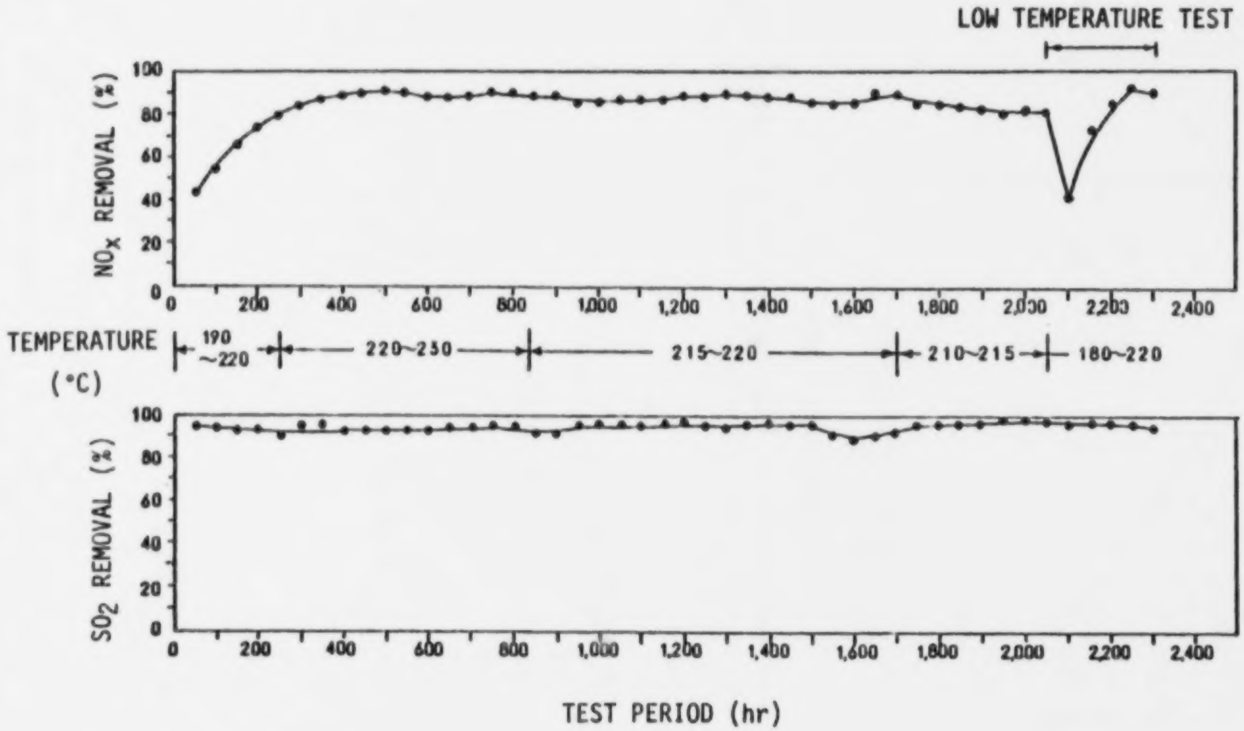

Figure 6-5. Continuous operation tests of the SHI carbon process for simultaneous removal of SO_x and NO_x.

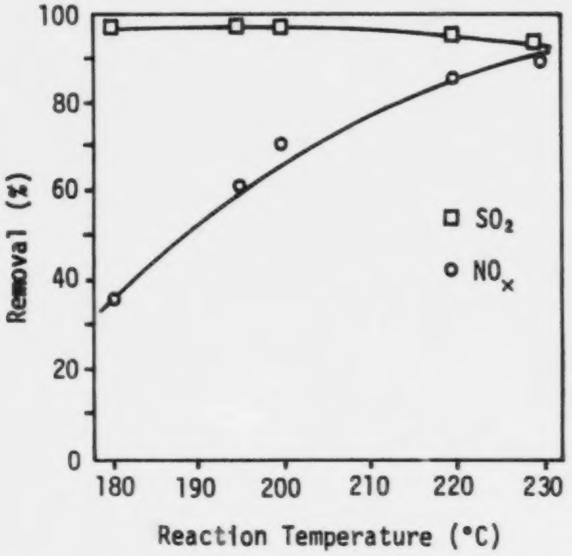

Figure 6-6. Effect of temperature on simultaneous removal of SO_x and NO_x with carbon (SO_2, 150-250 ppm; NO_x, 150-200 ppm; NH_3, 370 ppm; SV = 1000 hr^{-1}).

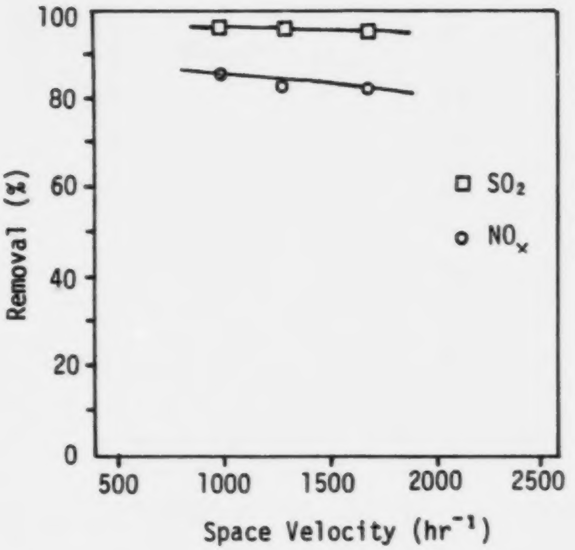

Figure 6-7. Effect of space velocity on simultaneous removal of SO_x and NO_x with carbon (SO_2, 150-200 ppm; NO_x, 150-200 ppm; NH_3, 370 ppm; 220°C).

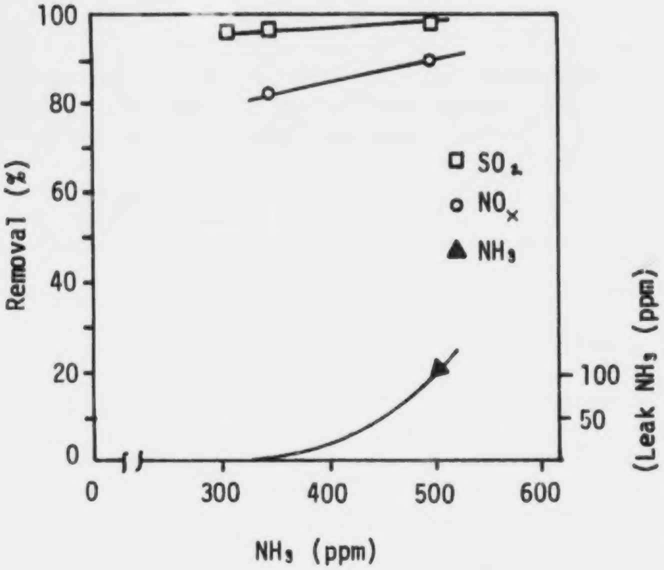

Figure 6-8. Effect of NH_3 added on simultaneous removal of SO_x and NO_x with carbon (NO_x, 150-200 ppm; SO_2, 150-250 ppm; SV, 1000 hr^{-1}; 220°C).

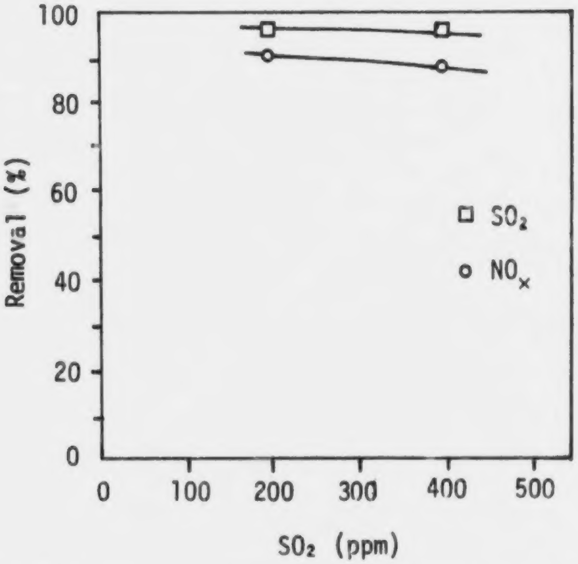

Figure 6-9. Effect of SO_2 on simultaneous removal of SO_x and NO_x with carbon (NO_x, 150-200 ppm; NH_3, 370 ppm; SV, 1000 hr^{-1}; 220°C).

TABLE 6-4. ESTIMATED COST FOR THE USE OF A FERRITE CATALYST FOR SIMULTANEOUS REMOVAL OF SO_x AND NO_x VERSUS THE USE OF SCR FOR THE FLUE GAS FROM A 500 MW COAL-FIRED BOILER*

	Simultaneous Removal (Activated Carbon)	SCR
Reaction Temperature	220°C	350°C
SO_2 Removal (percent)	95	--
NO_x Removal (percent)	90	90
Space Velocity (hr^{-1})	1000	5000
Catalyst Charge (tons)	1560	354
Catalyst Makeup (tons/year)	3000	295
Electric Power (kW)	3100	3300
NH_3 (kg/hr)	1050	760
LPG (kg/hr)	470	--
Steam (tons/hr)	1.0	0.6
Cooling Water (m^3/hr)	5.0	1.0
Maintenance Cost	2 percent/year of plant cost	2 percent/year of plant cost
Operator	2 men/shift	2 men/shift
Costs (millions of yen, $5000)		
Plant Cost Including Site Preparation and Control Room	5045	3033
Initial Catalyst Charge	1930	867
Total	6975	3900

* 1,845,000 Nm^3/hr of gas containing 500 ppm SO_2 and 600 ppm NO_x.

The investment cost for SCR is 7800 yen/kW (\$39/kW), but the cost for the simultaneous removal is 13,950 yen/kW (\$69.75/kW). Simultaneous removal is considerably less costly than the combination of SCR and conventional FGD; a plant by the combined system usually costs about 20,000 yen/kW (\$100/kW).

Three thousand tons of carbon catalyst would be consumed per year at a cost of 3.75 billion yen (\$18.75 million) per year, assuming a catalyst cost of 1.25 million yen/ton (\$6250/ton). For 7500 hours of operation per year, the cost of the carbon would be 1 yen/kWhr (\$0.005/kWhr), while depreciation of the plant cost for 7 years would be approximately 0.2 yen/kWhr (\$0.001/kWhr).

6.3.4 Evaluation

The simultaneous removal process is a simple modification of the activated carbon FGD process with thermal regeneration. The FGD process is fairly costly but the simultaneous removal process looks fairly promising because NO_x is removed by simple addition of ammonia. The greatest disadvantage of simultaneous removal is the enormous consumption of carbon, which is more expensive than the carbon for FGD. Since the consumption of carbon as well as that of inert gas and ammonia increases with the SO_2 content of the gas, the process should be used for flue gas containing a relatively small amount of SO_2, for example, a gas from burning a low-sulfur fuel. This gas would contain less than about 400 ppm of SO_x but would still require desulfurization. Even in this case, reduction of the carbon cost is desired.

The reactor can treat gases with particulate contents of up to about 200 mg/Nm^3. For flue gas from a coal-fired boiler, an electrostatic precipitator is needed ahead of the reactor to treat either the gas leaving the boiler economizer at about 400°C or the gas leaving an air preheater at 220-230°C. An additional air preheater may be needed after the reactor to recover the heat of the reactor effluent. There seems to be little problem with ammonium bisulfate in the air preheater after the reactor because more than 95 percent of the SO_x is caught by the carbon and the ammonia leakage is low.

6.4 UNITIKA ACTIVATED CARBON PROCESS FOR SIMULTANEOUS REMOVAL

6.4.1 Introduction

The engineering division of Unitika Co., one of the largest textile companies in Japan, has developed a dry simultaneous removal process for SO_x and NO_x which uses activated carbon. Since November 1975, they have operated a pilot plant which can treat 4500 Nm^3/hr of the flue gas from a glass melting furnace.

6.4.2 Process Description

The gas from the glass melting furnace contains a considerable amount of sodium sulfate vapor which contaminates the carbon catalyst. Therefore, the flue gas is first washed with a water spray to remove most of the sodium sulfate. The gas cooled to 60°C contains about 300 ppm SO_2, 200 ppm NO_x, and 5-10 mg/Nm^3 particulates.

The gas is heated to 250°C, injected with ammonia, and introduced into an adsorption tower (Figure 6-10). The adsorption tower has four compartments (reactors), each of which has a fixed carbon bed. One bed is regenerated while the other three operate in series to remove SO_2 and NO_x. About 400 ppm NH_3 is added to the gas at about 230°C and the gas mixture is led into three compartments. About 90 percent of the NO_x and SO_2 is removed.

The carbon that has absorbed SO_2 is heated to 350°C by an inert gas produced by incomplete combustion of propane. This gas contains 1-1.5

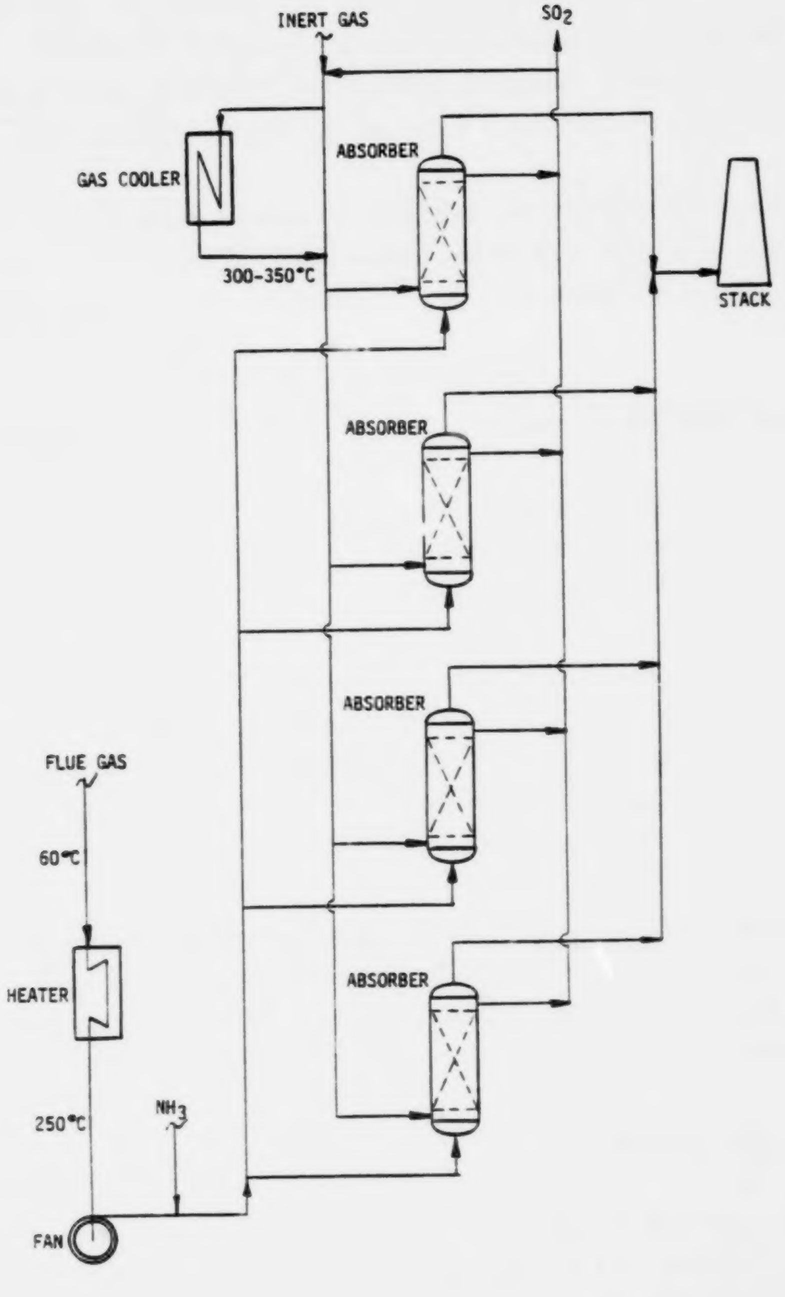
INERT GAS
SO2
GAS COOLER
ABSORBER
300-350°C
STACK
ABSORBER
ABSORBER
FLUE GAS
60°C
HEATER
ABSORBER
250°C
NH3
FAN

Figure 6-10. Flowsheet of the Unitika process for simultaneous removal of SO_x and NO_x.

percent CO, 9.5-10 percent CO_2, about 0.8 percent H_2 and 0.5 percent O_2. The recovered concentrated SO_2 gas can be used for sulfuric acid production or other purposes. Ammonium sulfate and bisulfate which tend to form on the carbon are decomposed to SO_2 and N_2 during regeneration.

The activated carbon, produced by Takeda Chemical for simultaneous removal, is in the form of cylinders with a 5 mm diameter and 8-10 mm length. Carbon consumption is estimated at about 50 percent of the charge per year.

The main design and operating parameters are as follows:

Tower Height	17 m
Carbon Bed Thickness	1 m
Pressure Drop	100 mmH_2O (reactor) 250 mmH_2O (total)
Absorption Time for One Cycle	3 days
Regeneration Time for One Cycle	12 hours
SO_2 in Gas From Regeneration Step	5-10 percent
Space Velocity (SV)	700-1500
Superficial Gas Velocity	0.1-0.2 m/sec

At an early stage of operation, the reaction temperature was about 180°C. At that temperature a large amount of ammonium bisulfate and sulfate formed on the carbon and caused plugging. Use of a 230°C temperature solved the problem.

6.4.3 Cost Estimation

The investment cost includes the initial charge of carbon (1.25 million yen/ton, \$6250/ton), and civil engineering work. The plant cost for the 500,000 Nm^3/hr plant is equivalent to 18,000 yen/kW (\$90/kW).

The operating cost was calculated for an industrial boiler with a flue gas temperature of 200°C operated for 95 percent of the total hours. The cost includes 7 years of depreciation and 10 percent interest.

6.4.4 Evaluation

The Unitika process is similar to the SHI process (Section 6.3) except that it uses a fixed bed. For flue gas containing little particulate matter, a fixed bed may be preferred because of the smaller consumption of carbon. The estimated yearly carbon consumption, 50 percent of initial charge for flue gas containing 1000 ppm of SO_x, is small compared with that by SHI (previous section), 113 percent of the charge for flue gas containing 150-250 ppm of SO_x. The estimate might be a little optimistic. Both Unitika and Sumitomo seem to use similar qualities of carbon and inert gas, and the difference in the carbon consumption may be too big to be attributed to the reactor types. Further studies may be needed on carbon consumption.

The process requires a considerable amount of fuel for heating the flue gas from 200 to 250°C. For the flue gas from utility boilers which normally is 150°C, the use of fuel to heat it to 250°C is too costly. Two air preheaters may be needed for a utility boiler; one between the boiler economizer and the reactor to cool the gas to 220-230°C and the other after the reactor for further heat recovery.

6.5 SHELL COPPER OXIDE PROCESS (SFGD PROCESS) FOR SIMULTANEOUS REMOVAL

6.5.1 Process Description[4]

The Shell process uses copper oxide supported on granular alumina in two parallel-passage reactors. The process was originally used only for SO_x removal. The reactions involved in the process are shown below:

TABLE 6-5. ESTIMATED COST FOR THE UNITIKA PROCESS FOR SIMULTANEOUS REMOVAL OF 1000 PPM SO_x AND 300 PPM NO_x BY ACTIVATED CARBON

	Capacity, 1000 Nm^3/hr		
	30	100	500
Investment Cost (10^6 yen, $5000)			
Major Units	248	587	2048
Accessories	41	87	252
H_2SO_4 Plant	111	226	700
Total	400	900	3000
Operating Cost (yen/kl oil, $0.005/kl)			
Depreciation and Interest	3700	2890	2440
Electric Power	650	650	650
Fuels*	2500	2500	2500
Ammonia	1200	1200	1200
Other**	1500	1400	1400
Total (yen/kl oil, $0.005/kl)	9550	8640	8190
(yen/kWhr, $0.005/kWhr)	2.12	1.92	1.82

* Kerosene for gas heating from 200 to 250°C and for heating for regeneration, and LPG to produce inert gas.

** Mostly for carbon.

$$CuO + SO_2 + \frac{1}{2} O_2 = CuSO_4 \qquad \text{(acceptance)} \qquad (6\text{-}17)$$

$$CuSO_4 + 2H_2 = Cu + SO_2 + 2H_2O \qquad \text{(regeneration)} \qquad (6\text{-}18)$$

$$Cu + \frac{1}{2} O_2 = CuO \qquad \text{(oxidation)} \qquad (6\text{-}19)$$

Flue gas at 400°C is introduced into one of the reactors, where SO_x reacts with copper oxide to form copper sulfate (reaction 6-17). Then hydrogen is introduced into the reactor to convert the copper sulfate to metallic copper and concentrated SO_2 which is used for sulfur or sulfuric acid production (reaction 6-18).

The two reactors are used alternately for acceptance and regeneration. Between the acceptance and regeneration, steam is injected to the reactor to purge the remaining flue gas or hydrogen. This eliminates any possibility of explosion. At the beginning of the acceptance flow, copper is oxidized by the oxygen in the flue gas and then reacts with SO_2 (reaction 6-19).

The Yokkaichi plant, Showa Yokkaichi Seikiyu (SYS), has treated flue gas (120,000 Nm^3/hr) from an oil-fired boiler since 1973. The plant reduces SO_x from about 1200 to 120 ppm. Since 1975, ammonia has been introduced into the reactor during the acceptance period to reduce NO_x. The process utilizes CuO and $CuSO_4$ as catalysts for the following selective reduction:

$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O \qquad (6\text{-}20)$$

Figure 6-11 shows the relation between NO_x in the reactor and the loading (α)--the mole ratio of $CuSO_4/(CuO + CuSO_4)$--when different amounts of NH_3 were used. The NO_x in the reactor effluent decreases (NO_x removal efficiency increases) as $CuSO_4$ increases, indicating that $CuSO_4$ works better than CuO as a catalyst.

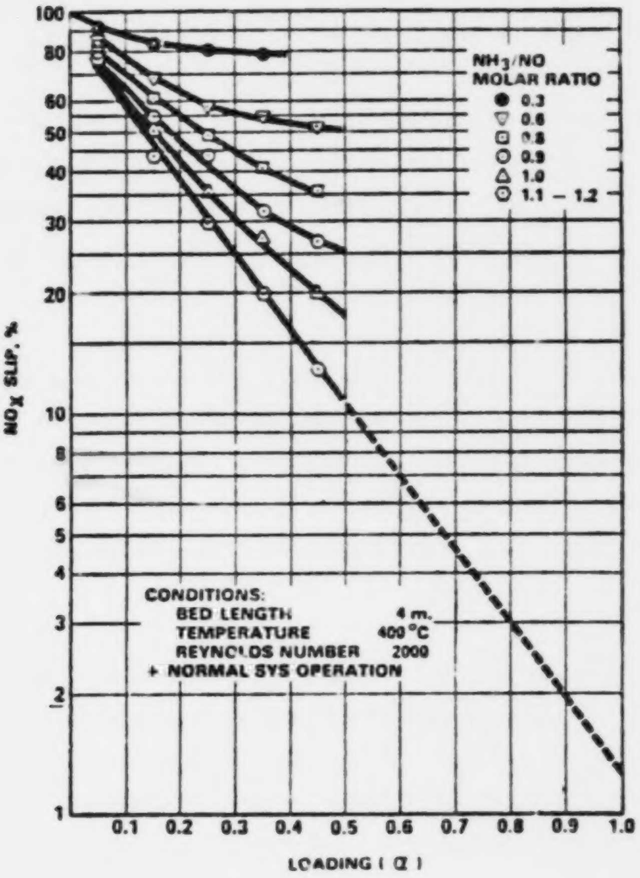

Figure 6-11. NO_x slip, percent of intake, versus loading, $CuSO_4/(CuO + CuSO_4)$ mole ratio, for a commercial SFGD acceptor/catalyst.

Figure 6-12 shows the relationship of NO_x conversion to NH_3/NO mole ratio at 0.4 mole SO_2/mole Cu (0.4 mole $CuSO_4$ + 0.6 mole CuO). The conversion rate reached 70 percent when 1 mole of NH_3 was used for each mole of NO.

Figure 6-13 shows the relation between the catalyst bed length (depth) and NO_x slip when $CuSO_4$ and a sufficient amount of NH_3 (1.1-1.5 mole NH_3 for each mole of NO) were used. A bed 4 meters deep can remove over 95 percent of the NO under such conditions.

Performance of the commercial SYS reactor is shown in Figure 6-14. At the beginning of acceptance, a considerable portion of copper is present as metal. This metal is not only inefficient for SO_x removal but also tends to oxidize NH_3 to NO_x. Cu is rapidly oxidized to CuO which readily reacts with SO_x. Ammonia is injected after Cu is converted to CuO.

The SO_2 removal efficiency reaches a maximum in about 20 minutes and then decreases as most of the CuO is converted to $CuSO_4$. NO_x removal efficiency continues to increase because $CuSO_4$ is a better catalyst than CuO. With an acceptance time of about 120 minutes, the overall removal efficiency reaches 88 percent for SO_x, 50 percent for NO_x with an NH_3/NO mole ratio of 0.71, and 65 percent for NO_x with a NH_3/NO mole ratio of 0.99.

The Yokkaichi palnt has removed about 90 percent of SO_2 and 40 percent of NO_x to meet local regulations. Leak ammonia present in the treated gas is only about 1 ppm at 40 percent removal. Operability of the plant which was not high for the first few years has been increased through improvements. Continuous operation for nearly one year was recently achieved.

6.5.2 Evaluation

The process is a desirable dry simultaneous removal process although it consumes considerable amounts of hydrogen and steam. Nearly 70 percent

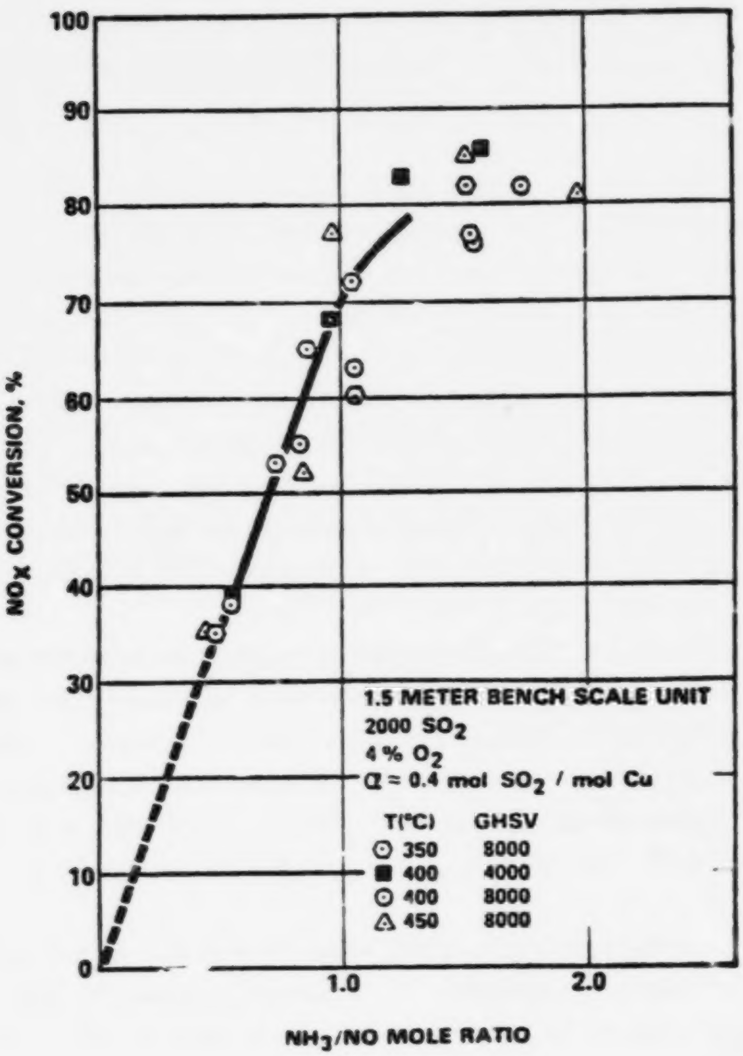

Figure 6-12. NO_x conversion versus NH_3/NO mole ratio for a commercial SFGD acceptor (SYS).

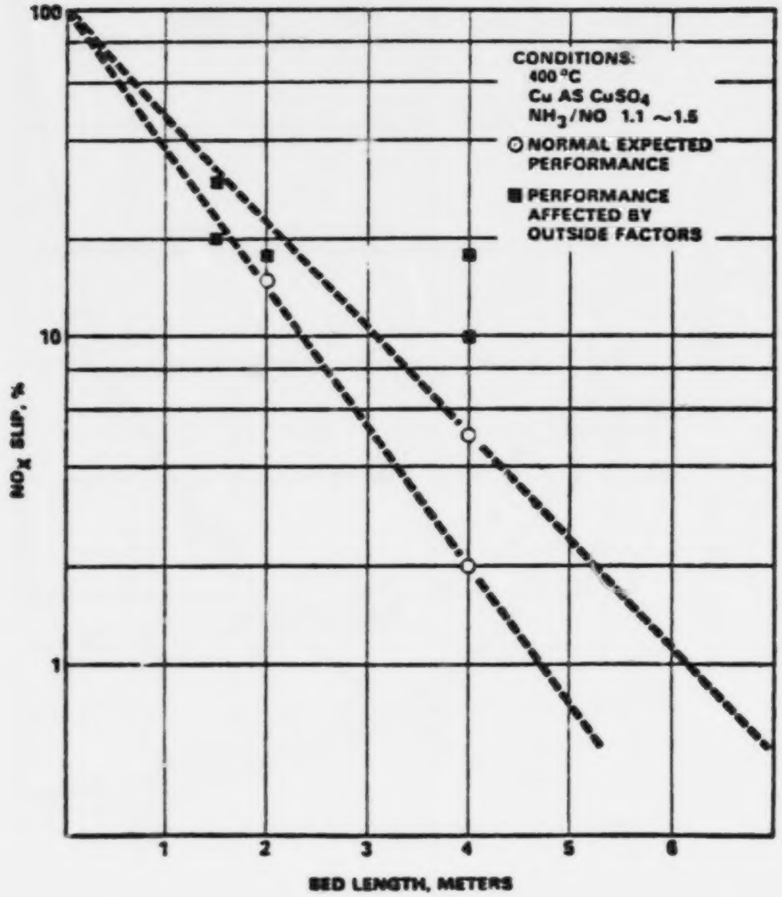

Figure 6-13. Unconverted NO_x as a function of catalyst bed length for a commercial SFGD acceptor (SYS) - upper and lower limits.

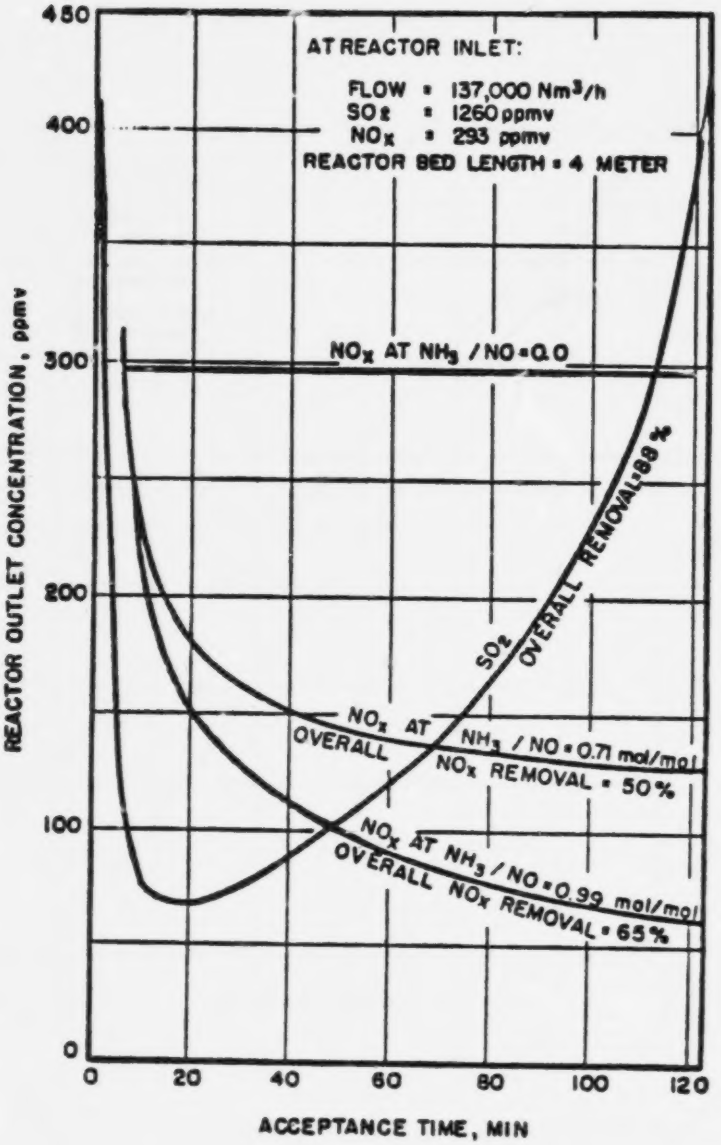

Figure 6-14. Performance of Shell FGD reactor at SYS, instantaneous SO_2 and NO_x slip (92).

NO_x removal with about 90 percent SO_2 removal is achieved by using an NH_3/NO mole ratio of 0.99. To obtain a higher NO_x removal efficiency, a larger reactor may be needed: a prolonged acceptance time increases the NO_x removal efficiency but lowers the SO_x removal efficiency, and the use of excessive ammonia would increase the ammonia leakage.

The process may be suitable for flue gas with a moderate SO_2 concentration. An SO_2-rich gas would require frequent switching between acceptance and regeneration which would cause the consumption of a large amount of hydrogen and steam and a decrease in NO_x removal efficiency.

The parallel-passage reactor is virtually free from dust plugging and may be useful for the flue gas from coal firing as well as from oil firing. The U.S. EPA recently awarded a contract for pilot scale (approximately 0.5 MW) studies of the Shell simultaneous removal process. Universal Oil Products (UOP) will operate the test unit which is to be sited at a coal-fired boiler at Tampa Electric Power Company's Big Bend Station in Florida.

6.6 EBARA ELECTRON BEAM RADIATION PROCESS FOR SIMULTANEOUS REMOVAL

6.6.1 Process Description [3]

A process for simultaneous removal of SO_x and NO_x with the use of an electron beam has been developed by Ebara Manufacturing Co. jointly with the Japan Atomic Energy Research Institute. It has been tested by Nippon Steel in a pilot plant which can treat 3000 Nm^3/hr flue gas. A flowsheet of the 1000 Nm^3/hr test plant of Ebara Manufacturing Co. is shown in Figure 6-15. The larger pilot plant of Nippon Steel went into operation in late 1977 to treat flue gas from an iron-ore sintering machine.

A flue gas at about 100°C to which a small amount of ammonia has been added is exposed to electron beam radiation. A powdery product consisting

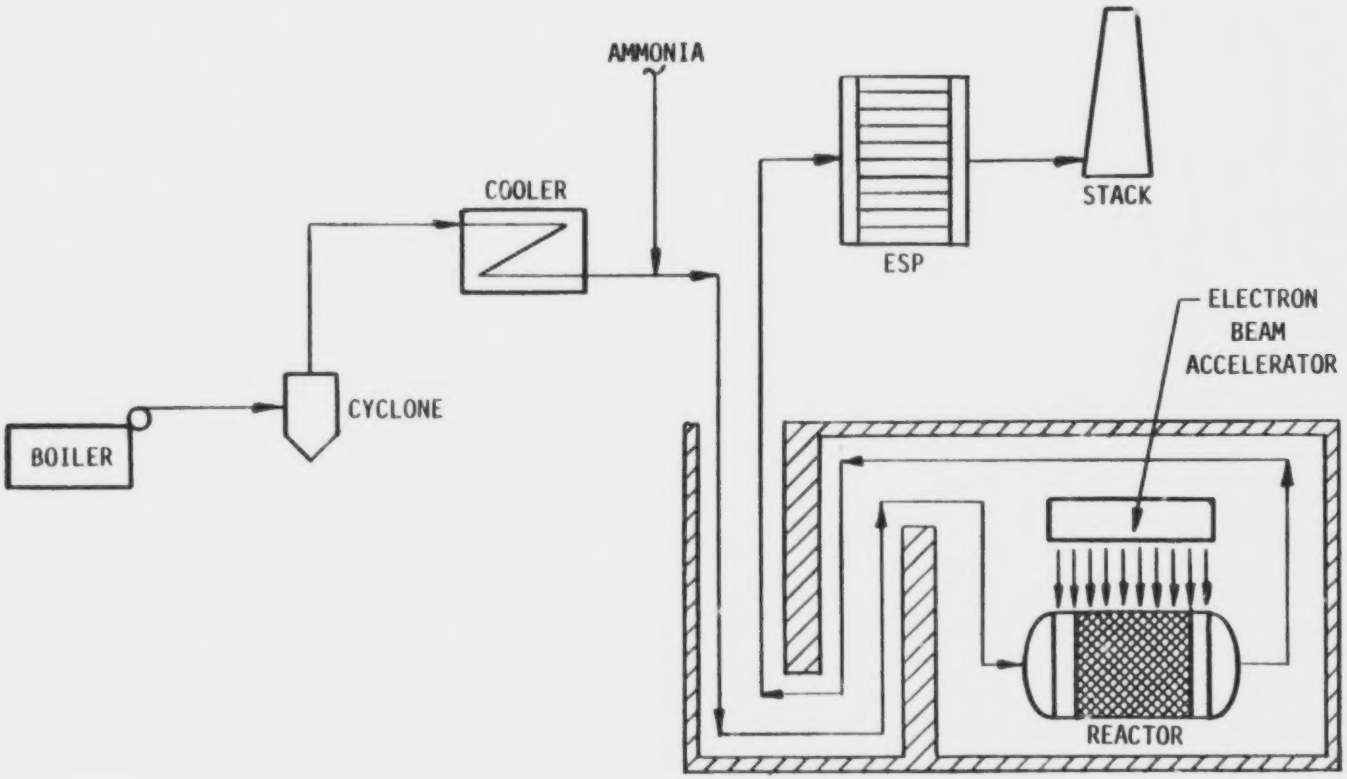
AMMONIA
COOLER
ESP
STACK
ELECTRON
BEAM
ACCELERATOR
CYCLONE
BOILER
REACTOR

Figure 6-15. Flowsheet of the 1000 Nm^3/hr electron beam radiation process pilot plant of Ebara Manufacturing Company.

of ammonium nitrate and sulfate is formed by the radiation in 1-5 seconds and is caught by an electrostatic precipitator. Although the reaction mechanism is not clear yet, the OH radical seems to play an important role.

Figure 6-16 shows test results of the process with flue gas at about 90°C containing 240 ppm NO_x, 220 ppm SO_x, 13 percent CO_2, 4 percent O_2, 9 percent H_2O and 0.1-0.2 g/Nm^3 particulates to which 700 ppm NH_3 was added. Although nearly 90 percent of the NO_x and SO_x was removed with an electron beam of 5 Mrad, about 80 percent removal with about 2 Mrad seems practical.

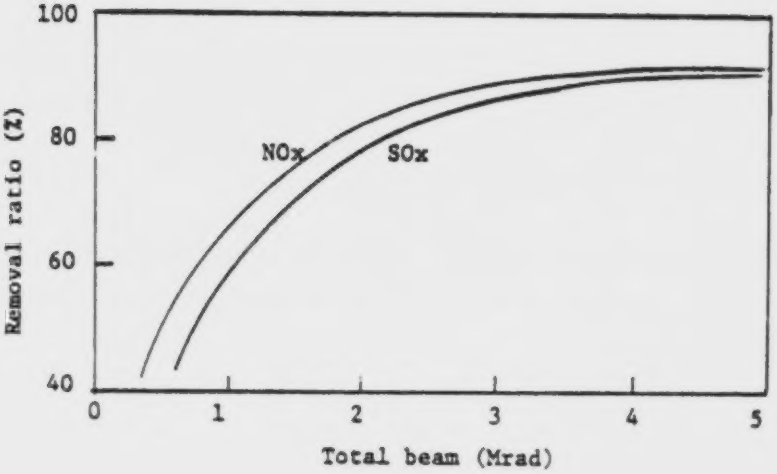

Figure 6-16. Removal ratios of SO_x and NO_x versus total beam for the electron beam radiation process used at the Ebara Manufacturing Company pilot plant.

6.6.2 Evaluation

Energy consumption is claimed to be not more than that of other simultaneous removal processes but the investment cost seems high. Many large electron beam generators are needed for a large-scale plant because the electron beam has a limited range. Another drawback of the process is that flue gas must be cooled to about 100°C; the removal efficiency is lower at the usual flue gas temperature of 150°C.

The process may suit gases at moderate flow rates and relatively rich in NO_x and low in SO_2 because the nitrogen content of the by-product is low when the gas is rich in SO_2. The by-product may be useful for use as fertilizer. When flue gas from a coal-fired boiler is treated, fly ash should be removed in advance to make the by-product ammonium salts useful for fertilizer.

6.7 OTHER DRY PROCESSES

6.7.1 Tests on Catalytic Decomposition of NO

The National Research Institute for Pollution and Resources has been testing catalytic decomposition of NO at 400-700°C jointly with Catalyst and Chemicals Industries.

Many kinds of catalysts based on aluminum and zeolite impregnated with alkalis, bases, and noble metals have been tested. Platinum and palladium (Pd) have shown an appreciable catalytic effect on the decomposition of NO to N_2 and O_2 as shown below:

		Decomposition Ratio, percent (SV = 3000)			
		400°C	500°C	600°C	700°C
Pt-Al_2O_3	(Pt 0.5 percent)	4.2	3.7	9.0	10.0
Pd-Al_2O_3	(Pd 0.5 percent)	0.0	0.0	10.0	27.0
Pt-Zeolite	(Pt 0.5 percent)	5.1	5.4	10.9	17.6
Pd-Zeolite	(Pd 2.0 percent)	4.5	6.1	11.0	--

The decomposition ratio, however, was not high. Even for a Pd catalyst at an SV of 500 hr^{-1} and a temperature of 700°C, the ratio was only 34 percent. Moreover, the catalysts are poisoned by many of the components of flue gas.

6.7.2 NO_x Recovery by Molecular Sieve

Nissan Chemical has installed an NO_x recovery plant with the PuraSiv N process developed by Union Carbide Corp., U.S. It treats 22,000 Nm^3/hr of flue gas from a nitric acid plant (160 tons HNO_3/day) containing 1000 ppm of NO_x. The plant was commissioned in May 1976 and has since been operated successfully. It reduces the NO_x concentration to below 50 ppm by molecular sieve adsorption. The adsorbed NO_x is thermally desorbed and returned to the nitric acid plant. By using the recovery system, the yield of the nitric acid plant has increased by 1 percent. The process seems very useful for treating tail gas from nitric acid plants.

6.8 REFERENCES

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2. Seki, M., *et al.*, Ammonium Hallide Activated Carbon Catalyst to Decompose NO_x in Stack Gas at Low Temperature Around 100°C. American Chemical Society, Chicago, August 1975. In English.

3. Present Status of Development of NO_x Abatement Technology by the Steel Industry Japan Steel Federation, April 1977.

4. Nooy, F. M., and J. B. Pohlenz, Nitrogen Oxides Reduction with the Shell Flue Gas Desulfurization Process. The Second Pacific Chemical Engineering Congress, Denver, August 1977. In English.

SECTION 7

WET PROCESSES FOR NO_x AND SIMULTANEOUS NO_x AND SO_x REMOVAL

7.1 GENERAL DESCRIPTION

7.1.1 Major Processes and Plants

Major commercial and test plants for NO_x and simultaneous NO_x and SO_x removal by wet processes are listed in Table 7-1. The plants are relatively small; the largest one has a capacity of 100,000 Nm^3/hr (33 MW equivalent).

The major wet processes may be classified as follows:

1) Oxidation-absorption

2) Absorption-oxidation

3) Oxidation-absorption-reduction (simultaneous removal of NO_x and SO_x)

4) Absorption-reduction (simultaneous removal of NO_x and SO_x)

Essentially all of the NO_x in the combustion gas is in the form of NO, which has poor reactivity and is not readily absorbed by most absorbents. NO is oxidized in NO_2 in air, but the oxidation occurs slowly. In processes (1) and (3) oxidizing agents are used to convert NO to NO_2 or N_2O_5 which are more readily absorbed. In the absorption oxidation process, NO is absorbed in a solution containing an oxidizing agent such as sodium

TABLE 7-1. MAJOR PLANTS FOR NO_x REMOVAL FROM FLUE GAS BY WET PROCESSES

Process Developer	Type of Process	Plant Owner	Plant Site	Capacity, Nm^3/hr	Source of Gas	Completion	By-Product
Tokyo Electric-Mitsubishi H.I.	Oxidation absorption	Tokyo Electric	Minami-Yokohama	2,000[a]	Boiler[b]	Dec 1973	HNO_3
Tokyo Electric-Mitsubishi H.I.	Oxidation absorption	Tokyo Electric	Minami-Yokohama	100,000[a]	Boiler[b]	Oct 1974	HNO_3
Kawasaki H.I.	Oxidation absorption	EPDC	Takehara	3,000[a]	Boiler[c]	Dec 1975	Gypsum, $Ca(NO_3)_2$
Nissan Engineering	Absorption oxidation	Ijima Metal	Tokyo	1,800	Pickling	July 1973	$NaNO_2$
Nissan Engineering	Absorption oxidation	Nissan Chemical	Toyama	3,000	HNO_3 Plant	Mar 1975	$NaNO_3$, NO
Mitsubishi Metal-MKK-Nihon Chem.	Absorption oxidation	Mitsubishi Metal	Omiya	4,000[a]	Boiler[d]	Dec 1974	KNO_3
Kobe Steel	Absorption oxidation	Kobe Steel	Kakogawa	1,000[a]	Furnace[e]	Dec 1973	Gypsum, N_2
Kobe Steel	Absorption oxidation	Kobe Steel	Kakogawa	50,000[a]	Furnace[e]	Mar 1976	Gypsum, N_2
Hodogaya	Absorption oxidation	Hodogaya	Koriyama	4,000[a]	Furnace[e]	Oct 1975	$NaNO_3$, NaCl
Sumitomo Metal-Fujikasui	Oxidation reduction	Sumitomo Metal	Amagasaki	62,000	Boiler[d]	Dec 1973	$NaNO_3$, NaCl, Na_2SO_4
Sumitomo Metal-Fujikasui	Oxidation reduction	Toshin Steel	Fuji	100,000	Furnace[f]	Dec 1974	$NaNO_3$, NaCl, Na_2SO_4
Sumitomo Metal-Fujikasui	Oxidation reduction	Sumitomo Metal	Osaka	39,000	Boiler[d]	Dec 1974	$NaNO_3$, NaCl, Na_2SO_4
Sumitomo Metal-Fujikasui	Oxidation reduction	Sumitomo Metal	Kashima	25,000[a]	Sintering machine	1976	Gypsum, $CaCl_2$, Ca, NO
Osaka Soda	Oxidation reduction	Osaka Soda	Amagasaki	60,000	Boiler[d]	Mar 1976	$NaNO_3$, NaCl, Na_2SO_4
Shirogane	Oxidation reduction	Mitsui Sugar	Kawasaki	48,000	Boiler[d]	Aug 1974	Na_2SO_4, $NaNO_3$
Chiyoda	Oxidation reduction	Chiyoda	Kawasaki	1,000[a]	Boiler[d]	1973	Gypsum, $Ca(NO_3)_2$
Mitsubishi H.I.	Oxidation reduction	Mitsubishi H.I.	Hiroshima	2,000[a]	Boiler[d]	Dec 1974	Gypsum, NH_3
Ishikawajima H.I.	Oxidation reduction	Ishikawajima H.I.	Yokahama	5,000[a]	Boiler[d]	Sept 1975	Gypsum, N_2
Kureha Chemical	Absorption reduction	Kureha Chem.	Nishiki	5,000[a]	Boiler[d]	Apr 1975	Gypsum, N_2
Chisso Corp.	Absorption reduction	Chisso P.C.	Goi	300[a]	Boiler[d]	1974	$(NH_4)_2SO_4$
Mitsui Engineering	Absorption reduction	Mitsui P.C.	Chiba	150[a]	Boiler[d]	1974	H_2SO_4, N_2
Asahi Chemical	Absorption reduction	Asahi Chemical	Mizushima	600[a]	Boiler[d]	1974	Gypsum, N_2

[a] Test plants; others are commercial plants.
[b] Gas-fired boiler.
[c] Coal-fired boiler.
[d] Oil-fired boiler.
[e] Iron-ore sintering machine.
[f] Metal-heating furnace.

or potassium permanganate, while in the absorption reduction process NO is absorbed in a liquor containing catalysts, as will be described in Section 7.1.4.

Little progress has been observed with wet processes in the past year. Many of the pilot plants have discontinued operation for the following reasons: 1) the processes are not as simple as selective catalytic reduction, and 2) many of the processes by-produce nitrates or ammonia. The Japanese fertilizer industry has suffered from excessive ammonia production capacity. Moreover, Japanese farmers have used little nitrate fertilizer because the major crop is paddy rice for which nitrate fertilizers are not suitable.

Some of the wet processes, however, are capable of removing NO_x and SO_x simultaneously and converting NO_x to nitrogen or ammonia which can be used for fertilizer in many other countries, in contrast to the dry processes which consume a considerable amount of ammonia. Existing FGD plants can be modified in order to remove NO_x simultaneously by adding a few vessels. It is desirable that the wet processes will be improved to produce a simpler system and more favorable economics.

7.1.2 Oxidizing Agents

Ozone (O_3) and chlorine dioxide (ClO_2) are used mainly for the oxidation of NO in the gaseous phase. They oxidize NO to NO_2 within a second but barely oxidize SO_2 to SO_3. Ozone can oxidize NO to N_2O_5 when added in excess.

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad (7\text{-}1)$$

$$2NO + 3O_3 \longrightarrow N_2O_5 + 3O_2 \qquad (7\text{-}2)$$

Ozone is fairly expensive; it costs 330 to 400 yen per kilogram and about 0.4 yen/kWh ($1.65 to $2.00/kg, $0.002/kWh) to treat a flue gas from a boiler containing 150 ppm of NO. A large scale ozone generator with a capacity of 100 kilograms per hour of ozone is near completion. It can treat about 230,000 Nm^3/hr of flue gas (76 MW equivalent) containing 200 ppm NO. The cost of ozone is expected to decrease to some extent with the large generator. The cost of chlorine dioxide is 30 to 40 percent lower than that of ozone, but chlorine dioxide introduces hydrochloric and nitric acids, which complicate the system.

$$2NO + ClO_2 + H_2O \longrightarrow NO_2 + HNO_3 + HCl \qquad (7\text{-}3)$$

Solutions of potassium and sodium permanganates, sodium and calcium hypochlorites, and hydrogen peroxide have been used for oxidation in the liquid phase, but these chemicals are also expensive.

7.1.3 Oxidation-Absorption and Absorption-Oxidation Processes

In oxidation-absorption processes the NO is first oxidized with a gaseous oxidizing agent and then absorbed. In absorption-oxidation processes the NO is absorbed in a solution containing an oxidizing agent. Usually NO_x absorption occurs more slowly in the latter case because NO must be absorbed in the liquor before it can be oxidized.

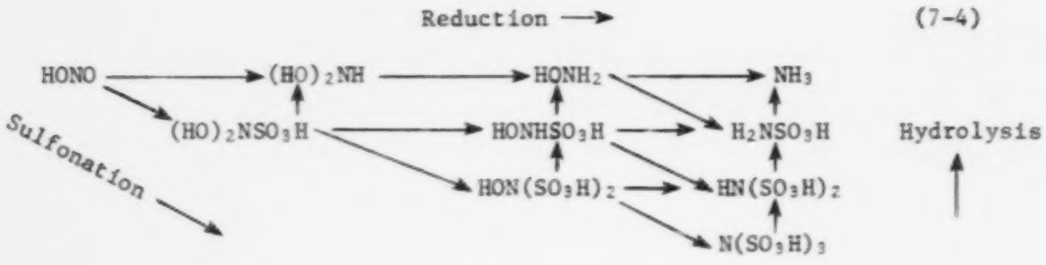
Most plants which use nitric acid for such processes as metal washing emit a gas fairly rich in NO_x (1000 to 10,000 ppm). However, the amount of gas is not great (500 to 5000 Nm^3/hr). In many of the plants, all or part of the NO is oxidized to NO_2, and the gas is absorbed in a sodium hydroxide solution. Activated carbon is used in some of the plants as a catalyst for NO oxidation by air. In other plants NO_x is absorbed in a solution containing an oxidizing agent such as NaClO or H_2O_2. In both cases the resulting liquor, containing nitrate and nitrite, is sent to a wastewater treatment system. Some plants use activated sludge treatment to reduce the nitrogen content of the water. Such processes cannot be applied on a large scale because the treatment does not sufficiently remove nitrogen compounds from the wastewater.

Tests were made in pilot plants to recover nitric acid for industrial use (see Section 7.2.2) or to recover potassium or calcium nitrate for fertilizer (see Sections 7.9.1 and 7.9.2). Those processes do not seem promising because of the high cost and the limited demand for the by-products.

7.1.4 Oxidation-Absorption-Reduction and Absorption-Reduction Processes (Simultaneous Removal)

Since 1973 many oxidation-absorption-reduction and absorption-reduction processes have been developed in which NO_x and SO_x are absorbed simultaneously. In the oxidation-absorption-reduction process, NO is first oxidized and then absorbed together with SO_x by lime/limestone scrubbing. In the absorption-reduction process NO is absorbed with SO_x in a liquor containing ferrous ion, which can form an adduct with NO. Usually EDTA (ethylenediamine tetraacetic acid, a chelating compound whose present cost in Japan is about 800,000 yen/t, $4000/t) is added to promote the reaction of ferrous ion with NO (Figures 7-1 and 7-2).[1]

In both cases, various reactions occur in the liquor or slurry and result in the reduction of NO_x by SO_2 (or sulfite) to NH_3 through imidodisulfonic acid ($HN(SO_3H)_2$), sulfamic acid (H_2NSO_3H), or a salt of either acid. The reaction sequence may be expressed in the following way.[2]



(7-4)

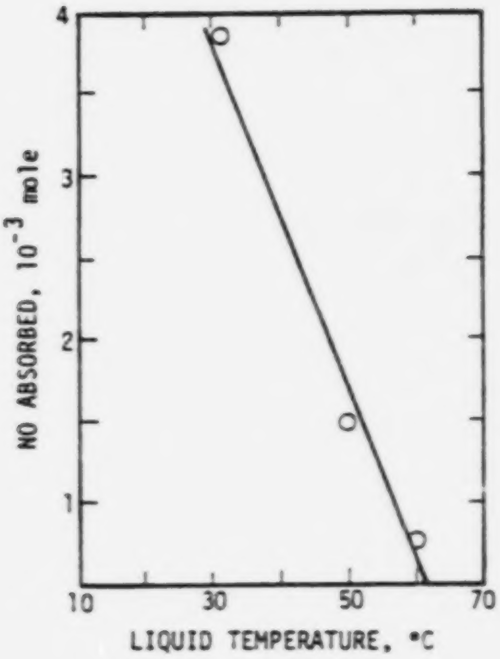


Figure 7-1. NO absorption in EDTA-Fe(II)liquor (0.01 mole/liter).*

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* Amount of liquor, 1 liter; gas flow, 1.5 liter/min; pH of liquor, 5.65; initial NO concentration, 275 ppm.

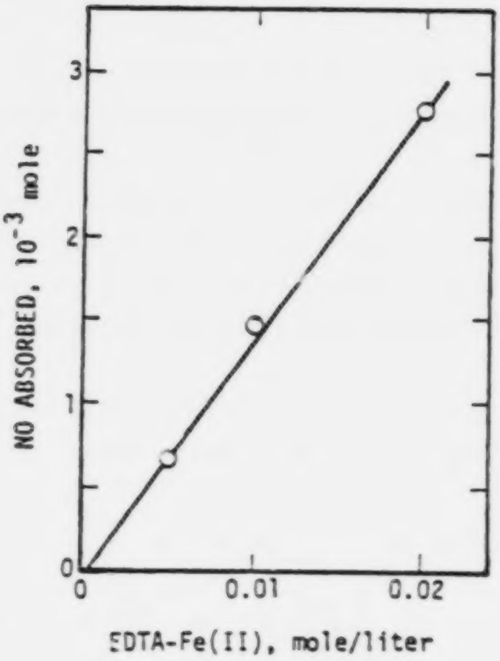

Figure 7-2. EDTA-Fe(II) concentration and NO absorption at 50°C.*

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* Amount of liquor, 1 liter; gas flow, 1.5 liter/min; pH of liquor, 5.65; initial NO concentration, 275 ppm.

Although the chemistry is complex, the overall reactions may be expressed simply in the following equations:

$$2NO_2 + 7SO_2 + 7CaCO_3 + 3H_2O = 7CaSO_4 + 2NH_3 + 7CO_2 \quad (7\text{-}5)$$

(oxidation reduction process, limestone scrubbing)

$$2NO + 5SO_2 + 8SO_2 + 8H_2O = 5(NH_4)_2SO_4 \quad (7\text{-}6)$$

(absorption reduction process, ammonia scrubbing)

The reactions indicate that 3.5 moles of SO_2 is needed for 1 mole of NO_2 and 2.5 moles of SO_2 is needed for 1 mole of NO. Since flue gas contains O_2 which oxidizes a considerable portion of SO_2 in a scrubber liquor, 4-5 moles of SO_2 is actually needed to attain 80 percent NO_x removal.

A portion of the NO_x can be reduced to N_2 in an aqueous solution. The reactions are complex but may be simply described as:

$$NH_2SO_3H + NO_2^- \longrightarrow N_2 + HSO_4^- + H_2O \quad (7\text{-}7)$$

Tanaka[2] has found that a compound $Na_2SO_3 \cdot 2NO$ is formed when NO is absorbed in an $NaSO_3$ solution. The compound is stable at a pH above 8, but it decomposes to form Na_2SO_4 and N_2O at lower pH. It is possible that in addition to N_2 or NH_3, N_2O also is formed in some of the wet processes.

$$Na_2SO_3 \cdot 2NO \longrightarrow Na_2SO_4 + N_2O \quad (7\text{-}8)$$

The presence of EDTA and ferrous ion prevents the formation of N_2O.

In some of the processes a considerable portion of the NO_x remains in the resulting liquor as nitrite and nitrate, which would cause a problem in wastewater treatment.

The advantage of such wet processes over dry processes is that they can simultaneously remove SO_2 and NO_x without the problems of particulates and ammonium bisulfate. They have not yet been commercialized on a large scale. Five relatively small commercial plants are in operation (Table 7-1).

7.2 MHI WET PROCESSES[3]

7.2.1 Introduction

Mitsubishi Heavy Industries (MHI), the leading FGD process developer and FGD plant constructor, has developed two wet processes for NO_x and simultaneous SO_x and NO_x removal, both using ozone as the oxidizing agent. The NO_x removal process uses water absorption to produce nitric acid; it was tested in cooperation with Tokyo Electric Power at Minamiyokohama Power Station. The simultaneous removal process uses lime/limestone scrubbing; it was tested at MHI's Hiroshima Research Institute.

7.2.2 Nitric Acid By-Production Process

A flowsheet of the process is shown in Figure 7-3. The flue gas (100,000 Nm^3/hr) from an LNG-fired boiler containing about 100 ppm NO_x is cooled with water spray, injected with ozone to oxidize NO to N_2O_5, and then washed with water in an absorber. More than 90 percent of the NO_x is removed when more than 1.7 moles of ozone are used for every mole of NO. An approximately 10 percent nitric acid solution is obtained which is concentrated to 60 percent for industrial use. The gas discharged from the absorber contains a small amount of ozone, which is removed by treatment with calcium sulfite slurry containing a small amount of catalyst. Major facilities of the plant are shown in Table 7-2.

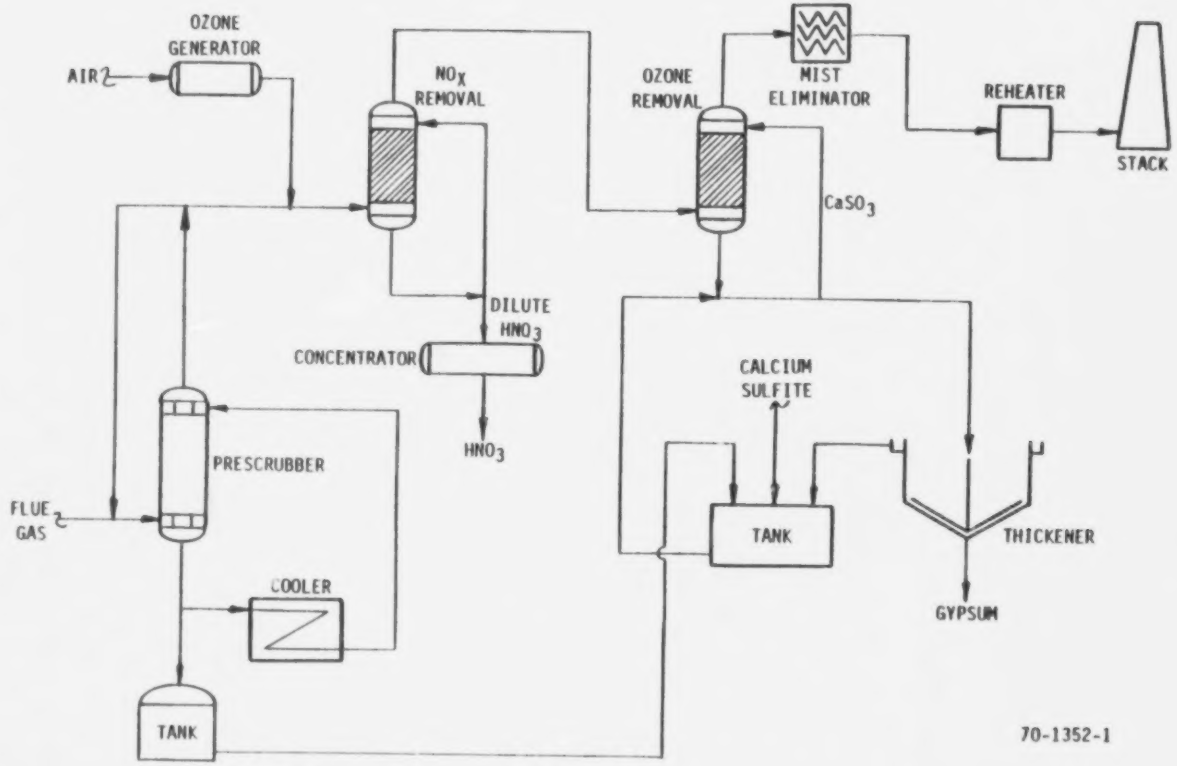
OZONE GENERATOR
AIR
NO_X REMOVAL
OZONE REMOVAL
MIST ELIMINATOR
REHEATER
STACK
$CaSO_3$
DILUTE HNO_3
CONCENTRATOR
HNO_3
CALCIUM SULFITE
PRESCRUBBER
FLUE GAS
TANK
THICKENER
COOLER
GYPSUM
TANK
70-1352-1

Figure 7-3. Flowsheet of Tokyo Electric-MHI oxidation absorption process.

TABLE 7-2. SPECIFICATIONS FOR THE TEST PLANT
(TOKYO ELECTRIC-MHI PROCESS)

	Material	Structure	Dimensions (m)
Prescrubber	SUS 304L	Packed Tower	4 x 4 x 11
NO_x Absorber	SUS 304L	Packed Tower	4 x 4 x 19.5
Ozone Absorber	SUS 304L	Packed Tower	4 x 4 x 19.5
Mist Eliminator	Polypropylene	Chevron	2.6 x 1.8 x 3
Blower	SS 60 (Impeller)	Centrifugal	370 kW

Operation parameters are listed in Table 7-3 and compared to those for the simultaneous removal plant. The nitric acid by-production process plant was operated for about 2 years beginning in late 1974 with virtually no problem. Ozone leaving the absorber in a small amount was entirely caught by the sulfite slurry and gypsum of good quality was by-produced. The process, however, is more costly than SCR which can be easily used for clean gas. The plant operation has been shut down.

7.2.3 Simultaneous Removal Process (Oxidation-Absorption-Reduction Process)

Another wet simultaneous removal process is a modification of the wet lime/limestone process as shown in Figure 7-4. Flue gas from an oil-fired boiler (2000 Nm^3/hr) is first cooled to 60°C by a prescrubber. Ozone is introduced into the flue gas prior to scrubbing. A water-soluble catalyst in a lime/limestone slurry is added to promote the oxidation of NO. More than 85 percent of the NO_x and more than 95 percent of the SO_2 are removed when more than 4 moles of SO_2 per mole of NO_x are present in the gas. The slurry discharged from the scrubber contains gypsum and a small amount of unreacted lime or limestone and soluble nitrogen-sulfur (N-S) compounds (reactions 7-9 - 7-11). The unreacted lime or limestone is treated with

TABLE 7-3. PILOT PLANTS BY MHI WET PROCESSES

	Nitric Acid By-Production	Simultaneous Removal
Gas Source	LNG-Fired Boiler	Oil-Fired Boiler
Capacity (Nm^3/hr)	100,000	2000
O_3/NO_x Mole Ratio	1.7-2.0	0.9-1.0
NO_x (inlet, ppm)	100	150-250
NO_x Removal (%)	Over 90	75-92
SO_2 (inlet, ppm)	None	500-1200
SO_2 removal (%)	--	90-99
Particulates (inlet, mg/Nm^3)	Trace	90-120
Prescrubber Type	Packed Tower	Spray Tower
Absorber Type	Packed Tower	Packed Tower
pH of Scrubber Liquor	Below 1	4-6
Ozone Remover Type	Packed Tower	--
By-Product	HNO_3, Gypsum	Gypsum
Year Completed	1974	1975

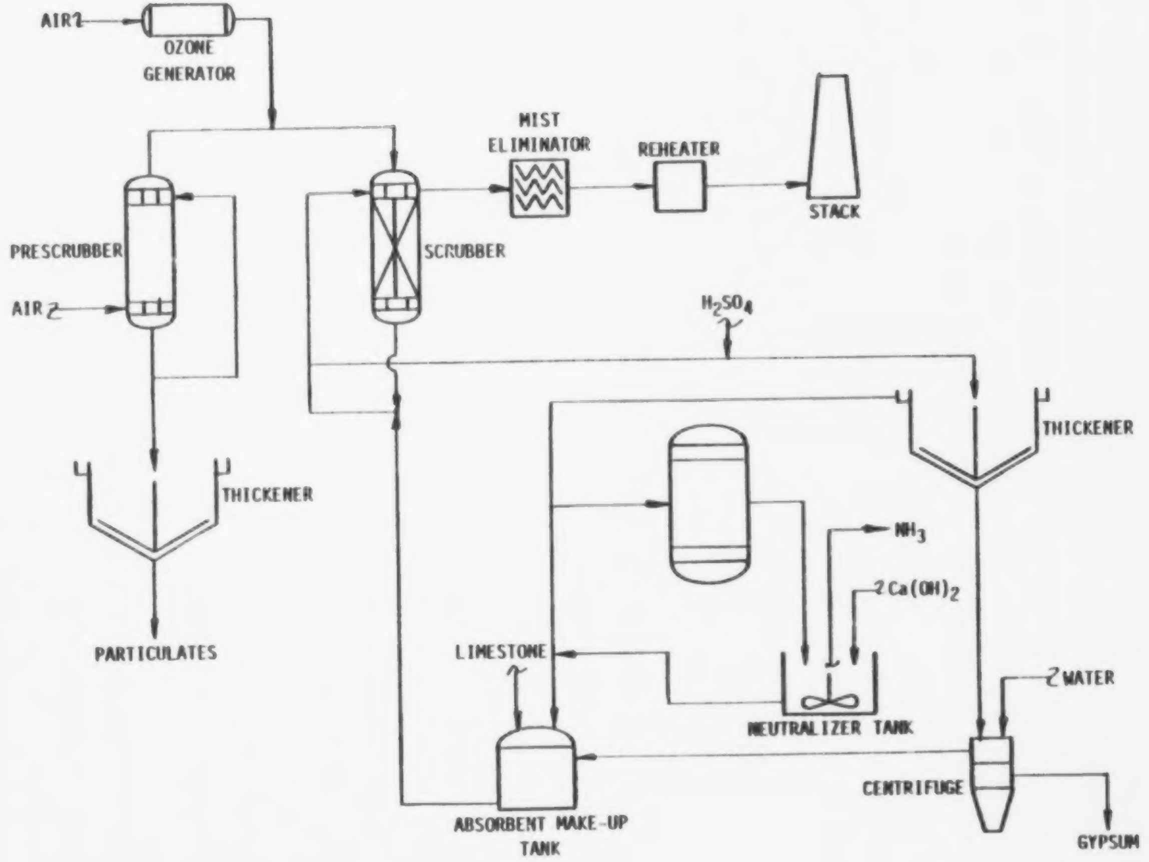
AIR
OZONE GENERATOR
MIST ELIMINATOR
REHEATER
STACK
PRESCRUBBER
AIR
SCRUBBER
H_2SO_4
THICKENER
THICKENER
NH_3
$Ca(OH)_2$
PARTICULATES
LIMESTONE
WATER
NEUTRALIZER TANK
CENTRIFUGE
ABSORBENT MAKE-UP TANK
GYPSUM

Figure 7-4. MHI simultaneous removal process.

sulfuric acid to increase the purity of by-product gypsum; the slurry is centrifuged to recover gypsum. Most of the liquor is returned to the absorber after lime or limestone is added; a small portion of the liquor is treated in a reactor at 100-130°C to decompose more than 95 percent of the N-S compounds (reactions 7-12 - 7-15). A small portion of the nitrogen is converted to N_2; most of it is converted to NH_4HSO_4 which is then treated with lime to recover gypsum and gaseous ammonia. The gypsum and ammonia, 5-10 percent concentration, may be recovered and used (reaction 7-16).

$$\begin{aligned} &2NO_2 + Ca(OH)_2 + CaSO_3\cdot\tfrac{1}{2}\,H_2O + \tfrac{1}{2}\,H_2O \longrightarrow \\ &\quad Ca(NO_2)_2 + CaSO_4\cdot 2H_2O \end{aligned} \tag{7-9}$$

$$\begin{aligned} &Ca(NO_2)_2 + 4(CaSO_3\cdot\tfrac{1}{2}H_2O) + 2H_2O \longrightarrow \\ &\quad 2CaNOH(SO_3)_2 + 3Ca(OH)_2 \end{aligned} \tag{7-10}$$

$$\begin{aligned} &CaNOH(SO_3)_2 + CaSO_3\cdot\tfrac{1}{2}H_2O + \tfrac{3}{2}\,H_2O \longrightarrow \\ &\quad CaNH(SO_3)_2 + CaSO_4\cdot 2H_2O \end{aligned} \tag{7-11}$$

$$\begin{aligned} &2Ca[NOH(SO_3)_2] + 2H_2O \longrightarrow \\ &\quad Ca(NOH\cdot HSO_3)_2 + Ca(HSO_4)_2 \end{aligned} \tag{7-12}$$

$$\begin{aligned} &Ca(NOH\cdot HSO_3)_2 + 2H_2O \longrightarrow \\ &\quad \tfrac{2}{3}\,N_2 + CaSO_4\cdot 2H_2O + \tfrac{2}{3}\,NH_4HSO_4 + \tfrac{1}{3}H_2SO_4 \end{aligned} \tag{7-13}$$

$$\begin{aligned} &2Ca[NH(SO_3)_2] + 2H_2O \longrightarrow \\ &\quad Ca(NH_2SO_3)_2 + Ca(HSO_4)_2 \end{aligned} \tag{7-14}$$

$$\begin{aligned} &Ca(NH_2SO_3)_2 + Ca(HSO_4)_2 + 4H_2O \longrightarrow \\ &\quad 2NH_4HSO_4 + 2CaSO_4\cdot 2H_2O \end{aligned} \tag{7-15}$$

$$\begin{aligned} &NH_4HSO_4 + Ca(OH)_2 \longrightarrow \\ &\quad NH_3 + CaSO_4\cdot 2H_2O \end{aligned} \tag{7-16}$$

Some of the operation data of the pilot plant are listed in Table 7-3. Specifications of the plant facilities are shown in Table 7-4.

TABLE 7-4. SPECIFICATIONS OF 2000 NM^3/HR TEST PLANT FOR SIMULTANEOUS REMOVAL OF SO_x AND NO_x BY OXIDATION-ABSORPTION-REDUCTION

Prescrubber	Spray Tower	0.7 m diameter, 7 m height
Absorber	Grid Packed Tower	0.5 m diameter, 13 m height
Ozonizer	Mitsubishi Electric (OS-1200)	1200 g/hr*
Flue Gas Fan	Capacity 5000 Nm^3/hr	Pressure, 600 mm H_2O
Centrifuge	Basket Type	300 l/hr

* About half of the capacity is sufficient for the pilot plant.

The plant has been operated without appreciable problem. Nearly 1 mole of O_3 has been used for each mole of NO to obtain 85-90 percent NO_x removal efficiency. It is possible to obtain over 90 percent efficiency by using a larger amount of O_3. In this case, however, a small amount of nitrate is formed in the liquor, which makes wastewater treatment difficult. Unreacted ozone is entirely removed in the scrubber by the calcium sulfite slurry. There is no leakage of O_3 from the system.

Because of the oxidizing effect of NO_2 and O_3, virtually all of the sulfite is oxidized to gypsum in the scrubber. An oxidizing tower, which is usually installed for conventional lime/limestone gypsum processes, is not needed when the SO_2 content of flue gas is below 1200 ppm. For flue gas richer in SO_2, an oxidizer may be needed but should be substantially smaller than those in conventional FGD plants.

Gypsum derived from the sulfuric acid is less than 5 percent of the total by-product gypsum. Sulfuric acid is not needed when a high purity of gypsum is not required.

Both capital and operation costs for a commercial simultaneous removal process plant to treat flue gas from an oil-fired boiler containing about 150 ppm of NO_x are estimated by MHI to be about 40 percent higher than those for an SO_2 removal process plant. About 80 percent of the increased costs are due to the ozone generator.

7.2.4 Evaluation

A desirable feature of the by-product nitric acid process is that NO_x is converted to a useful by-product. The process, however, seems fairly costly and requires a large amount of ozone and many vessels. Moreover, it may not be applied to SO_x-containing gas. For NO_x removal from clean gas, SCR may be easier and less costly.

The simultaneous removal process is a fine process in which both NO_x and SO_2 are removed by the simple addition of ozone to the gas and a catalyst to the scrubber liquor. It is easy to modify the existing lime/limestone FGD plant for simultaneous removal.

A large disadvantage of the process is the high cost of ozone. The process may be useful for flue gas with a relatively low NO_x concentration such as that from an oil-fired boiler, but may be too expensive for an NO_x-rich gas such as that from a coal-fired boiler. Recovery of the by-product ammonia should be considered. The ammonia may be injected into the boiler to reduce NO_x. The simultaneous removal process may be applied to flue gas from a coal-fired boiler if NO_x concentration is reduced to 250 ppm by combustion control and to below 150 ppm by injecting the by-product ammonia into the boiler.

As in the case of conventional FGD processes, some wastewater would have to be purged to prevent the accumulation of impurities from the gas and lime or limestone. The recovery of catalyst from the wastewater may present a problem.

7.3 IHI OXIDATION-ABSORPTION-REDUCTION PROCESS (SIMULTANEOUS REMOVAL)

7.3.1 Introduction

Ishikawajima-Harima Heavy Industries (IHI), one of the largest producers of boilers, ships, and machines, has developed a wet simultaneous removal process with ozone oxidation and lime/limestone scrubbing to by-produce gypsum which converts NO_x to N_2. A pilot plant which can treat 5000 Nm^3/hr flue gas from an oil-fired boiler was operated in 1976 and 1977.

7.3.2 Process Description

A flowsheet of the IHI process is shown in Figure 7-5. Flue gas is cooled, injected with ozone to convert NO to NO_2, and treated in a scrubber with a lime/limestone slurry at pH 5-6 containing small amounts of $CuCl_2$ and NaCl as catalysts. Over 80 percent of the NO_x and over 95 percent of the SO_2 are absorbed at an L/G of over 8 liters/Nm^3. Most of the absorbed NO_x forms calcium sulfamate, a soluble compound (reaction 7-20), while a small portion of NO_2 is converted into various forms (reactions 7-21 - 7-24).

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 + H_2O \qquad (7\text{-}17)$$

$$SO_2 + CaCO_3 \longrightarrow CaSO_3 + CO_2 \qquad (7\text{-}18)$$

$$SO_2 + CaSO_3 + H_2O \longrightarrow Ca(HSO_3) \qquad (7\text{-}19)$$

$$2NO_2 + 5CaSO_3 + Ca(HSO_3) + 11H_2O \longrightarrow Ca(NH_2SO_3)_2 + 5(CaSO_4 \cdot 2H_2O) \qquad (7\text{-}20)$$

$$2NO_2 + 4CaSO_3 + 8H_2O \longrightarrow N_2 + 4(CaSO_4 \cdot 2H_2O) \qquad (7\text{-}21)$$

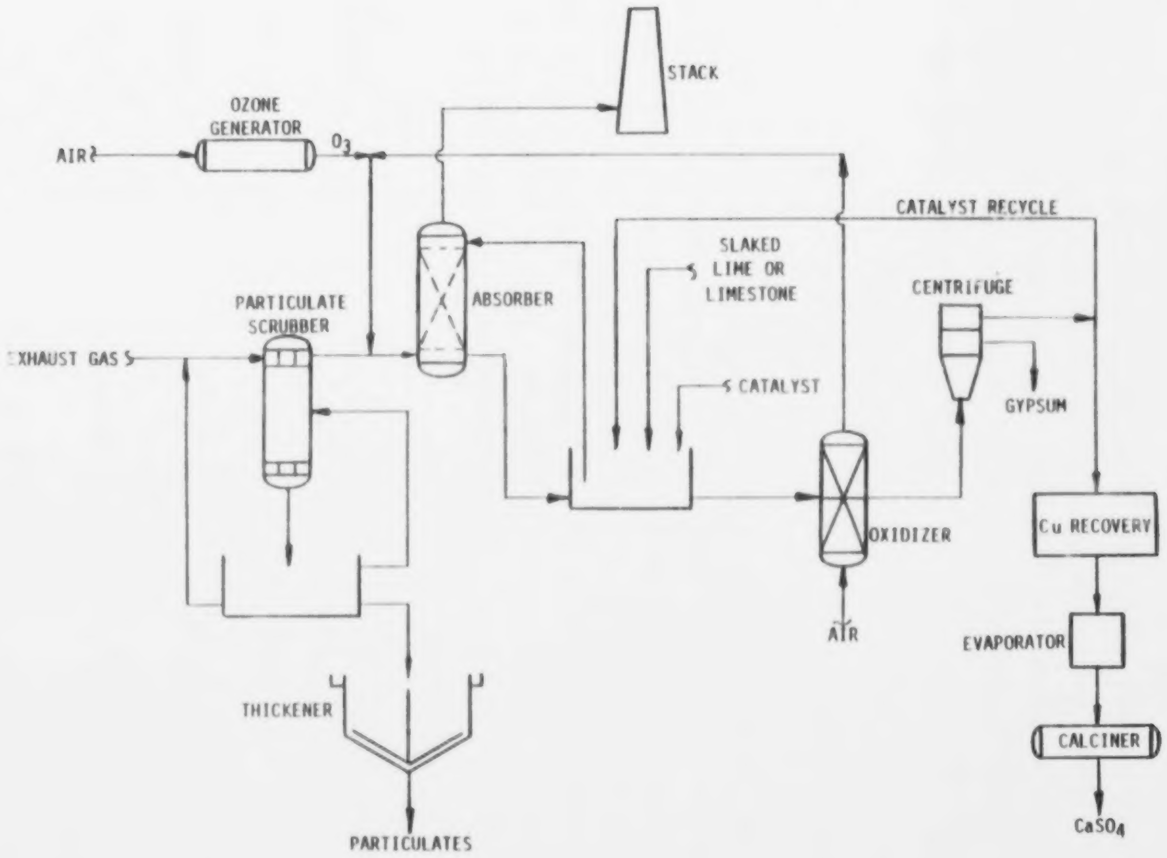
STACK
OZONE GENERATOR
AIR
O_3
CATALYST RECYCLE
SLAKED LIME OR LIMESTONE
CENTRIFUGE
PARTICULATE SCRUBBER
ABSORBER
EXHAUST GAS
CATALYST
GYPSUM
OXIDIZER
Cu RECOVERY
AIR
EVAPORATOR
THICKENER
CALCINER
PARTICULATES
$CaSO_4$

Figure 7-5. Flowsheet of the IHI process.

$$4NO_2 + 4CaSO_3 + 2H_2O \longrightarrow Ca(NO_2)_2 + Ca(NO_3)_2 + 2Ca(HSO_3)_2 \qquad (7\text{-}22)$$

$$2NO_2 + 3CaSO_3 + 6H_2O \longrightarrow N_2O + 3(CaSO_4 \cdot 2H_2O) \qquad (7\text{-}23)$$

$$Ca(NO_2)_2 + Ca(NH_2SO_3)_2 + 2H_2O \longrightarrow 2N_2 + 2(CaSO_4 \cdot 2H_2O) \qquad (7\text{-}24)$$

The relation between the catalyst concentration and NO_x removal efficiency is shown in Figure 7-6. The combination of $CuCl_2$ and NaCl is effective for NO_x removal. Figure 7-7 shows the effect of pH on SO_x and NO_x removal with and without the catalyst. A high pH increases SO_x removal but lowers NO_x removal. A pH between 5 and 6 is optimum for simultaneous removal.

The slurry leaving the absorber is treated with air bubbles if necessary to complete the oxidation of $CaSO_3$ to gypsum. The gypsum slurry is filtered to obtain a good quality by-product gypsum. Most of the liquor discharged from the centrifuge is returned to the absorber; the rest is sent to a thermal decomposition step after separation of copper by lime addition.

For the thermal decomposition, the liquor is first evaporated and dried to crystallize calcium sulfamate and nitrate. These are then calcined with limestone in a rotary kiln at about 900°C to produce calcium sulfate and nitrogen gas (reactions 7-25 and 7-26).

$$\begin{aligned} &2Ca(NH_2SO_3)_2 + 4CaCO_3 + 2Ca(HSO_4)_2 + 3O_2 + 2H_2O \longrightarrow \qquad (7\text{-}25) \\ &\qquad 2N_2 + 8CaSO_4 + 4CO_2 + 8H_2O \end{aligned}$$

$$Ca(NO_3)_2 + Ca(NH_2SO_3)_2 \longrightarrow 2N_2 + 2CaSO_4 + O_2 + 2H_2O \qquad (7\text{-}26)$$

The pilot plant was operated without appreciable problem. IHI also developed a process to hydrolize the sulfamate to by-produce ammonia. In

CONDITIONS

CONCENTRATION OF $CaSO_3$: 5 wt%
pH OF LIQUOR : 5.5
$NO_2/(NO + NO_2)$: 0.95

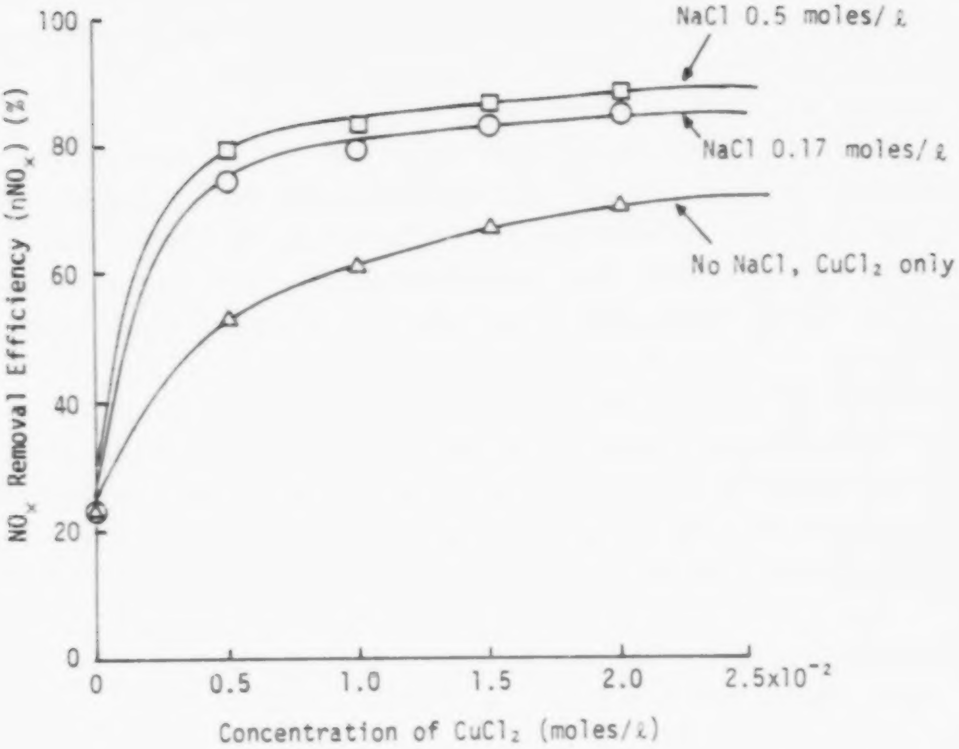

Figure 7-6. Effect of $CaCl_2$ and NaCl concentration on NO_x removal efficiency in the IHI process.

CONDITIONS

CONCENTRATION OF $CaSO_3$: 5 wt%
CONCENTRATION OF $CuCl_2$: 0.01 mole/ℓ
CONCENTRATION OF NaCl : 1 wt%
$NO_2/(NO + NO_2)$: 0.95

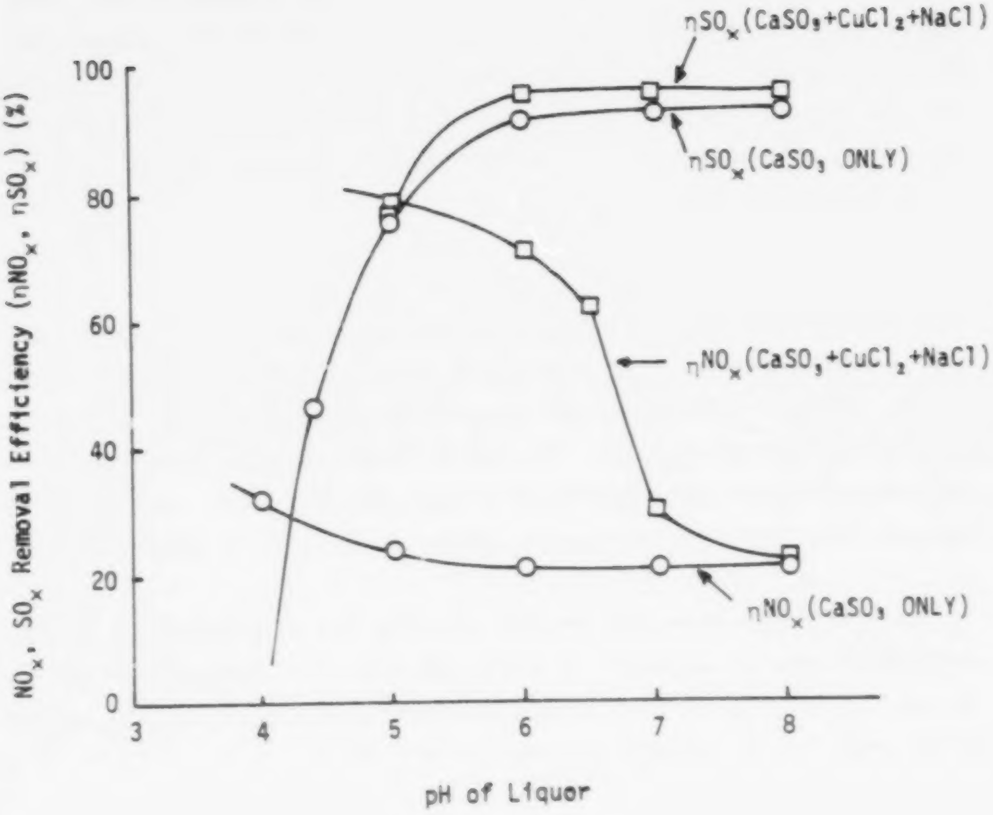

Figure 7-7. Effect of pH on SO_x and NO_x removal efficiency in the IHI process.

this case, calcium nitrate accumulates in the scrubber liquor and has to be separated.

7.3.3 Economics

Figure 7-8 shows investment cost and operating cost for the simultaneous removal of SO_x and NO_x for 8000 hours of annual operation. The figures include 7 years' depreciation. Roughly speaking, both investment and operation costs are about 40 percent more than those of FGD only. The figure also shows the incremental operating cost for NO_x removal (the difference between simultaneous removal and FGD). The operation costs may be considerably higher for NO_x-rich flue gas from a coal-fired boiler because a much larger amount of ozone may be needed.

7.3.4 Evaluation

IHI made extensive fundamental studies of the IHI process. The pilot plant was operated without appreciable problem and proved the reliability of the process. However, there is no plan yet to install a commercial plant based on the process. The major reason for this hesitance is the current policy of power companies to use LNG or low-sulfur oil for new boilers with selective catalytic reduction (SCR) of NO_x without FGD.

For flue gas from high-sulfur oil, the IHI process might be more economical than a combination of SCR and wet FGD. The process may not be useful for flue gas from a coal-fired boiler because the large amount of ozone required would make the process too costly.

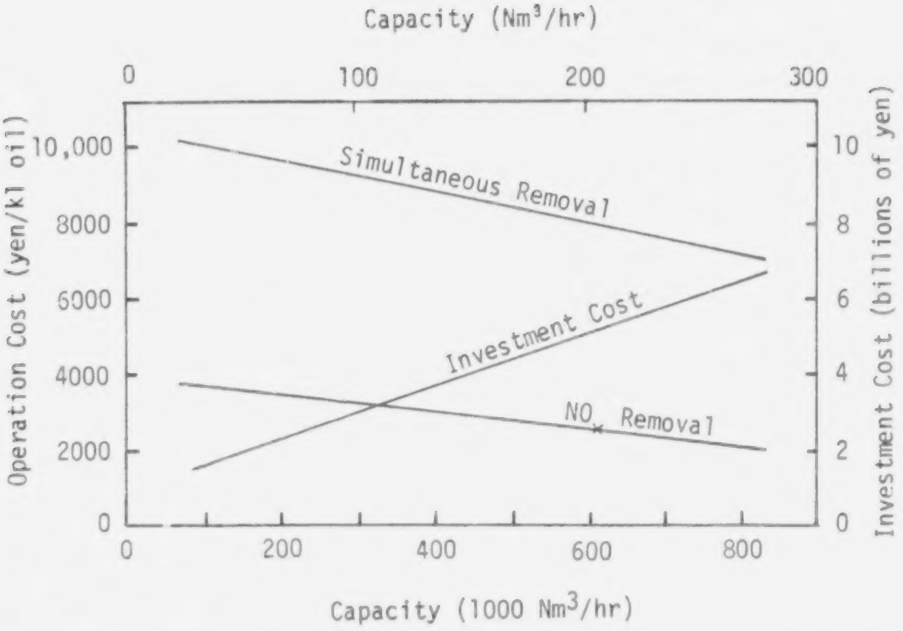

Figure 7-8. Investment and operation costs.*

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* Inlet SO_x, 1500 ppm; inlet NO_x, 180 ppm; yearly operation, 8000 hours.

7.4 SUMITOMO-FUJIKASUI PROCESS (MORETANA PROCESS)

7.4.1 Introduction

Sumitomo Metal, one of the largest steel producers, jointly with Fujikasui Engineering, a pollution control plant engineering and construction company, has developed a wet simultaneous removal process which uses ClO_2 as the oxidizing agent and NaOH as the absorbent. They have constructed relatively small commercial plants using the process. The process can remove over 90 percent of the SO_x and NO_x but it may not be suitable for large plants. A large amount of NaOH is consumed and the waste liquor containing sodium chloride, nitrate and sulfate must be treated.

Sumitomo and Fujikasui recently developed a modified process which uses ClO_2 as the oxidizing agent and a $CaCO_3$ slurry containing a catalyst as the absorbent. After tests with a small pilot plant, Sumitomo Metal has operated since 1976 a larger pilot plant which can treat 25,000 Nm^3/hr of flue gas from an iron-ore sintering machine at the Kashima Works.

7.4.2 ClO_2-$CaCO_3$ Process[4]

A flowsheet of the simultaneous removal process which uses ClO_2 and $CaCO_3$ is shown in Figure 7-9. The flue gas contains about 200-250 ppm NO_x, 250-500 ppm SO_x, 15-18 percent O_2, and 30-80 mg/Nm^3 particulates. The gas (25,000 Nm^3/hr) is first treated with water in a Moretana tower, an improved type of perforated plate tower, to remove most of the particulates and to cool and humidify the gas. The gas is then injected with ClO_2 gas to oxidize NO to NO_2 by the following reaction.

$$2NO + ClO_2 + H_2O \longrightarrow NO_2 + HCl + HNO_3 \qquad (7\text{-}27)$$

A stoichiometric amount of ClO_2 is added to instantaneously oxidize virtually all of the NO to NO_2. SO_2 in the gas is not oxidized by ClO_2.

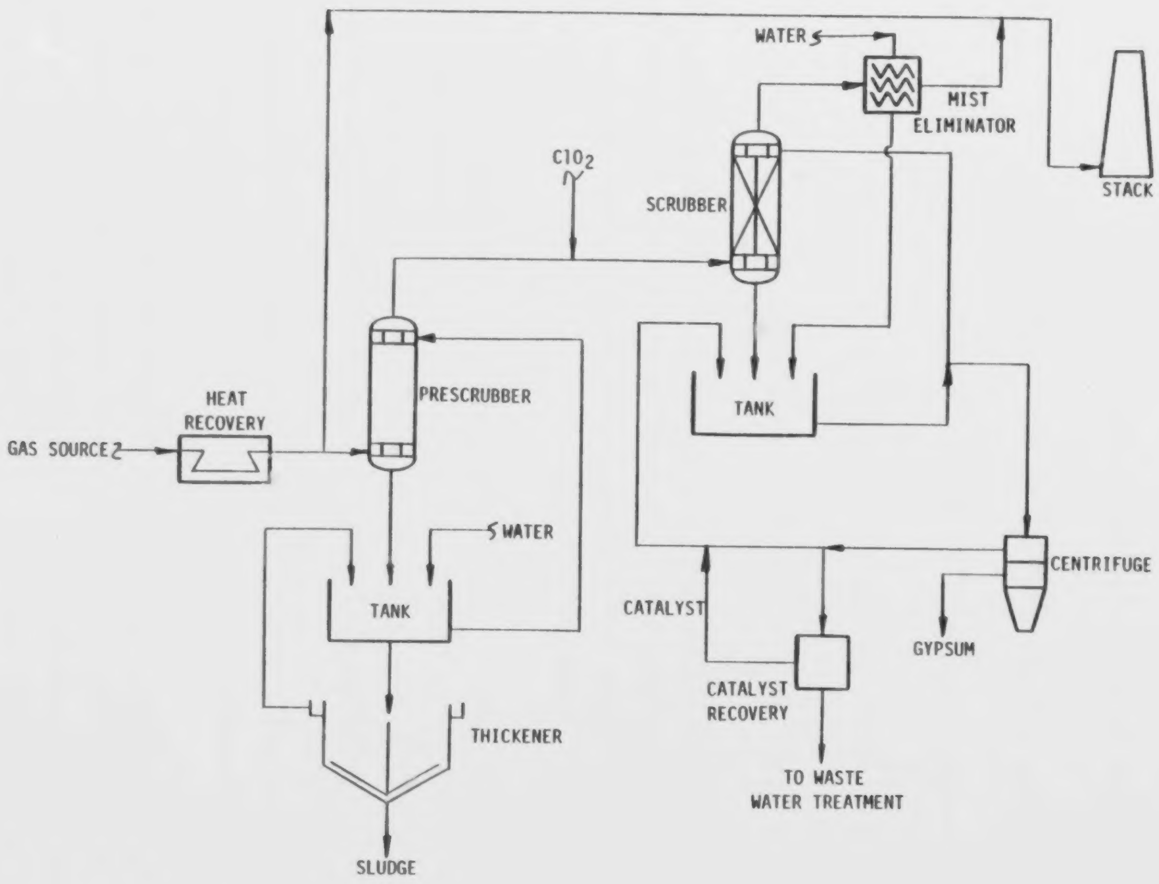
WATER
MIST
ELIMINATOR
STACK
ClO_2
SCRUBBER
PRESCRUBBER
HEAT
RECOVERY
GAS SOURCE
TANK
WATER
TANK
CENTRIFUGE
CATALYST
GYPSUM
CATALYST
RECOVERY
THICKENER
TO WASTE
WATER TREATMENT
SLUDGE

Figure 7-9. Flowsheet of the Sumitomo-Fujikasui ClO_2-$CaCO_3$ process.

The gas is then treated in another Moretana tower (scrubber) with a limestone slurry containing a catalyst. The following reactions occur in the scrubber.

$$CaCO_3 + SO_2 \longrightarrow CaSO_3 + CO_2 \qquad (7\text{-}28)$$

$$2NO_2 + 4CaSO_3 \xrightarrow{\text{Catalyst}} N_2 + 4CaSO_4 \qquad (7\text{-}29)$$

$$2HNO_3 + 5CaSO_3 \xrightarrow{\text{Catalyst}} N_2 + 5CaSO_4 + H_2O \qquad (7\text{-}30)$$

$$2HNO_3 + CaCO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2 \qquad (7\text{-}31)$$

$$2HCl + CaCO_3 \longrightarrow CaCl_2 + H_2O + CO_2 \qquad (7\text{-}32)$$

The treated gas leaving the scrubber contains 60-80 ppm NO_x, 25-50 ppm SO_x, 15-18 percent O_2, and 20-40 mg/Nm^3 particulates. The gas is passed through a mist eliminator and led to a stack. The total pressure drop of the gas in the system is 500 mmH_2O.

Most of the slurry leaving the scrubber is recirculated, but a portion is centrifuged to separate gypsum, which is of high quality and useful for cement and wallboard. About 150 liters/hr of the liquor from the centrifuge are sent to a wastewater treatment system after most of the catalyst in the liquor is recovered and returned to the scrubber. Limestone and a small amount of makeup catalyst are added to the remaining liquor before it is sent to the scrubber.

The waste liquor contains calcium chloride and nitrate. It can be dried in a spray dryer to give a powdery product that may be useful for production of an anti-freezing agent. It is also possible to treat the liquor with ammonium sulfate to precipitate gypsum and obtain a liquor containing ammonium chloride and nitrate that may be used as liquid fertilizer. The small amount of catalyst remaining in the product is not toxic and the product has no harmful effect on the environment.

7.4.3 Evaluation

An advantage of this simultaneous SO_x/NO_x removal process is that a plant can be constructed simply by adding a wastewater treatment system to a conventional wet limestone scrubbing plant.

The pilot plant has removed about 80 percent of the NO_x and over 90 percent of the SO_x. It may be possible to remove 90 percent of the NO_x and over 95 percent of the SO_x by using two scrubbers in series. Removal of over 90 percent of the NO_x is difficult with other wet simultaneous removal processes. It is possible with the Moretana process because half of the NO is oxidized to form HNO_3 which is readily absorbed by the limestone slurry; removal of 80 percent of the NO_2 formed by the oxidation results in an overall removal of 90 percent.

On the other hand, the waste liquor contains large amounts of nitrate and chloride. The use of these by-products is limited. Although the process may be better than the ClO_2-NaOH process, disposal of the waste liquor or the by-product from the liquor may not be easy. The ClO_2-NaOH process not only consumes a large amount of NaOH but also produces a waste liquor containing sodium chloride, sulfate and nitrate.

A considerable amount of ClO_2 has been used in Japan as a bleaching agent. For treating a large amount of flue gas, ClO_2 should be produced at the plant. Though this is not difficult, it does require an electrolytic cell, NaOH and HCl, and may not be convenient for power plants.

Ozone can be used as the oxidizing agent in place of ClO_2. Sumitomo and Fujikasui have preferred ClO_2 to ozone because ClO_2 is considerably less expensive than ozone. When ozone is used, the by-products of the process are gypsum and calcium nitrate. A considerable amount of the nitrate may be used for fertilizer or it can be treated with ammonium sulfate to produce gypsum and ammonium nitrate. For flue gas that is not rich in NO, ozone may be used instead of ClO_2 to simplify the system.

7.5 CHISSO ENGINEERING ABSORPTION REDUCTION PROCESS (CEC PROCESS) FOR SIMULTANEOUS REMOVAL

7.5.1 Introduction

Chisso Engineering is a subsidiary of Chisso Corp., a large chemical company which produces petrochemicals and fertilizers. Chisso has developed a wet simultaneous removal process in which the gas is scrubbed with an ammonia solution containing EDTA and the ferrous ion. A pilot plant which can treat 300 Nm^3/hr flue gas from an oil-fired boiler has been operated since 1975. NO_x in the gas is converted to NH_3 by the reducing effect of SO_2 to produce ammonium sulfate. The reactions are complex but the overall reaction may be simply expressed as follows:

$$2NO + 5SO_2 + 8NH_3 + 8H_2O = 5(NH_4)_2SO_4 \qquad (7\text{-}33)$$

The process has been licensed to Catalytic, Inc., U.S.A.

7.5.2 Process Description[5]

The flue gas is first subjected to water scrubbing for cooling and removal of particulates and chlorine, and then is treated in a scrubber with an ammonia solution at pH 6.0 (Figure 7-10). The main reactions are shown below:

$$SO_2 + (NH_4)_2SO_3 + H_2O \longrightarrow 2NH_4HSO_3 \qquad (7\text{-}34)$$

$$NO + 3NH_4HSO_3 \longrightarrow NH(SO_3NH_4)_2 + \tfrac{1}{2}(NH_4)_2S_2O_6 + H_2O \qquad (7\text{-}35)$$

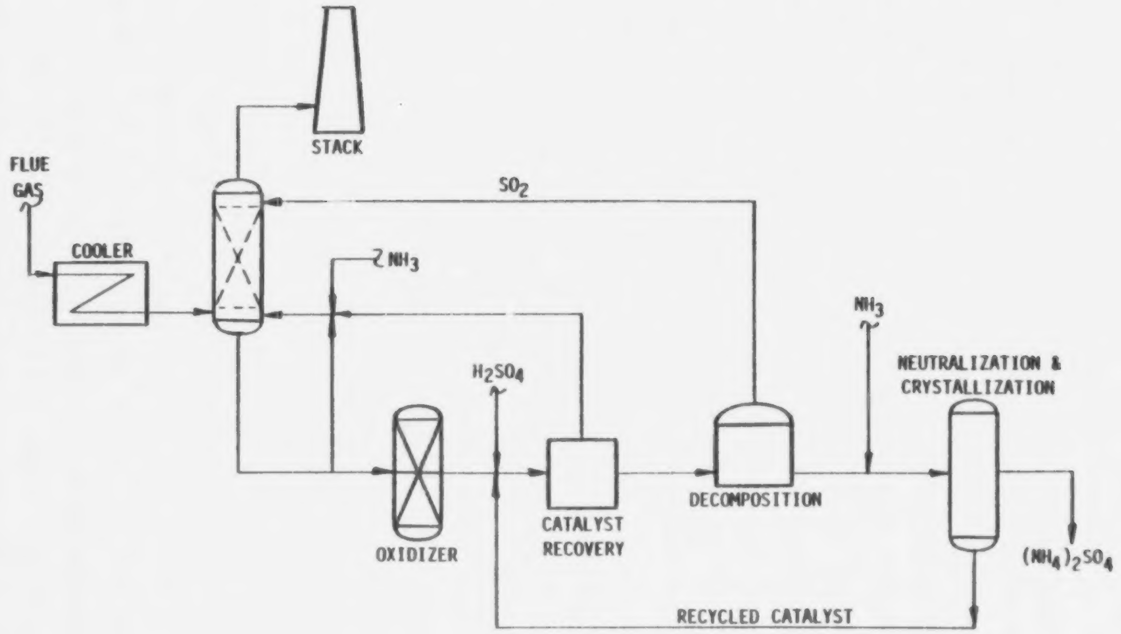
FLUE GAS
COOLER
STACK
SO_2
NH_3
H_2SO_4
NH_3
NEUTRALIZATION & CRYSTALLIZATION
OXIDIZER
CATALYST RECOVERY
DECOMPOSITION
$(NH_4)_2SO_4$
RECYCLED CATALYST

Figure 7-10. Flowsheet of the CEC process.

$$2NH_4HSO_3 + \frac{1}{2}O_2 \longrightarrow (NH_4)_2S_2O_6 + H_2O \qquad (7\text{-}36)$$

$$(NH_4)_2SO_3 + \frac{1}{2}O_2 \longrightarrow (NH_4)_2SO_4 \qquad (7\text{-}37)$$

To obtain a high NO_x removal ratio, about 5 moles of SO_2 are needed for each mole of NO. Normally 70-85 percent of the NO_x is removed with more than 99 percent of the SO_2 in a scrubber with about 20 stages of perforated plates. A portion of the scrubber liquor is subjected to air bubbling to oxidize ammonium sulfite and bisulfite to sulfate and dithionate. Then sulfuric acid is added to the liquor to lower the pH to 0.5. The acidic liquor is cooled to 0 ∿ -5°C by the latent heat of evaporation of liquid ammonia. About 90 percent of EDTA is crystallized by the cooling. The EDTA is centrifuged and returned to the absorber. The liquor discharged from the centrifuge is then heated under 3 atmospheres of pressure at 120-130°C for several hours to decompose imidodisulfonate and dithionate. Reactions 7-38, 7-39 and 7-40 occur because of the heating in the acidic liquor (Figure 7-11). A considerable portion of the remaining EDTA is also decomposed in the decomposition step.

$$NH(SO_3NH_4)_2 + H_2O \longrightarrow NH_2SO_3NH_4 + NH_4HSO_4 \qquad (7\text{-}38)$$

$$NH_2SO_3NH_4 + H_2O \longrightarrow (NH_4)_2SO_4 \qquad (7\text{-}39)$$

$$(NH_4)_2S_2O_6 \longrightarrow (NH_4)_2SO_4 + SO_2 \qquad (7\text{-}40)$$

SO_2 released by reaction 7-40 is returned to the scrubber. This is done to maintain an adequate NO_x/SO_2 ratio and to reduce SO_2 emissions. The liquor obtained from the decomposition step contains ammonium sulfate and bisulfate with small amounts of dithionate, EDTA and the ferric ion. The liquor is neutralized with ammonia and concentrated in a circulation flash evaporator after the separation of ferric hydroxide. The crystallized ammonium sulfate is centrifuged; the mother liquor containing dithionate

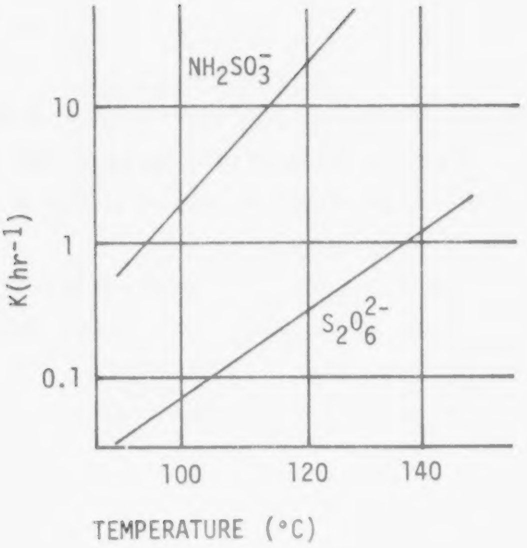

Figure 7-11. Decomposition rates of intermediates in the CEC process.*

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* $-d(S_2O_6^{2-})/dt = k(S_2O_6^{2-})$

$-d(NH_2SO_3^-)/dt = k(NH_2SO_3^-)$

with small amounts of EDTA and chloride is returned to the catalyst recovery step.

About 70 percent of the sulfur and 10-20 percent of the nitrogen in the by-product ammonium sulfate are derived from the SO_2 and NO_x of the flue gas and the rest from sulfuric acid and ammonia added to the system.

7.5.3 Economics[6]

Chisso Engineering considers the plant cost for the process to be 20 to 30 percent lower than the total of wet process FGD and dry process denitrification. The estimated operating costs are shown in Table 7-5.

The estimated costs are 7289 yen/kl ($36.4/kl) or 1.82 yen/kWhr ($0.0091/kWhr) for a plant which can treat 150,000 Nm^3/hr (50 MW) and 6593 yen/kl ($33.0/kl) or 1.65 yen/kWhr ($0.0083/kWhr) for a 500,000 Nm^3/hr plant (166 MW), excluding the cost for gas reheating.

7.5.4 Evaluation

Production of ammonium sulfate from recovered NO_x and SO_2 is an advantage of the process. A major disadvantage may be the requirement of a large scrubber with about 20 stages of perforated plates. The gas pressure drop is about 30 mmH_2O for each stage. Oxygen concentration of the gas affects the NO_x removal efficiency. For a gas containing 500 ppm NO and 2500 ppm SO_2, the NO_x removal efficiency would be about 80 percent for 3 percent O_2 and 70 percent for 5 percent O_2.

The plume problem common to ammonia scrubbing FGD processes has not been encountered with the CEC process, presumably because of the unusually high SO_x removal efficiency of over 99 percent.

TABLE 7-5. ESTIMATED OPERATING COSTS (CEC PROCESS FOR OIL FIRED BOILER)

Basis:	Plant Size	150,000 Nm^3 (Dry)/hr (O_2, 4 percent)
	Fuel Oil Burned	12.5 kl/hr (Sulfur, 3 weight percent)
	Stream Time	8000 hours/year
	NO_x Absorption Ratio	80 percent (200 ppm → 50 ppm)

	Consumption Per Hour	Unit Price	Cost Per Kl Oil
Utility			
Electric Power	1800 kWhr	8.5 yen/kWhr ($0.042/kWhr)	1224 yen/kl ($ 6.12/kl)
Steam	6000 kg	2.2 yen/kg ($0.011/kg)	1056 yen/kl ($ 5.28/kl)
Cooling Water	700 m^3	4.0 yen/m^3 ($0.02/$m^3$)	223 yen/kl ($ 1.12/kl)
Process Water	10 m^3	16.0 yen/m^3 ($0.08/$m^3$)	12 yen/kl ($ 0.06/kl)
Total			2515 yen/kl ($12.575 kl)
Ammonia and Chemicals			2493 yen/kl ($12.465/kl)
Labor Cost, 10 men x 5 M yen/man-year			500 yen/kl ($ 2.50/kl)
Depreciation, Interest, Maintenance, Taxes, Insurance			3660 yen/kl ($18.30/kl)
Recovered Ammonium Sulfate 1700 kg/hr x 15 yen/kg (Return)			1880 yen/kl ($ 9.40/kl)
Net Operating Cost			7289 yen/kl ($36.445/kl)*

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* For a 500,000 Nm^3/hr plant: 6593 yen/kl ($32.965/kl). Cost for flue gas reheating is not included above.

The process would be useful where there is a good market for ammonium sulfate and where the removal of 70-80 percent of the NO_x is required. Where there is no market for the sulfate, it should be decomposed either by addition of lime to the sulfate liquor to precipitate gypsum or by the IFP process to recover elemental sulfur. By these processes, ammonia is regenerated and returned to the scrubbing system.

A portion of the ammonia is derived from the NO_x and must be discharged from the system. One disposal method is to inject the ammonia into the boiler at 900-1000°C for further reduction of NO_x. With these processes, refrigeration is needed for cooling the liquid in the catalyst recovery step because latent heat of evaporation of liquid ammonia would not be available.

7.6 ASAHI CHEMICAL PROCESS

7.6.1 Introduction

The environmental division of Asahi Chemical, one of the largest chemical companies in Japan, has developed wet simultaneous removal processes based on sodium and potassium scrubbing, both using EDTA and the ferrous ion. The entire system was tested at a small pilot plant which could treat 40-60 Nm^3/hr of flue gas; the scrubbing and thermal decomposition steps were tested with larger facilities equivalent to 500-600 Nm^3/hr. The potassium process can remove over 90 percent of the NO_x with over 99 percent of the SO_x, but it seems costly. The sodium process, capable of removing 80-90 percent of the NO_x with 99 percent of the SO_x, may be more practical. The sodium process will be described below.

7.6.2 Process Description

A flowsheet of the sodium process is shown in Figure 7-12. Flue gas is first treated by water scrubbing to remove particulates and chlorine

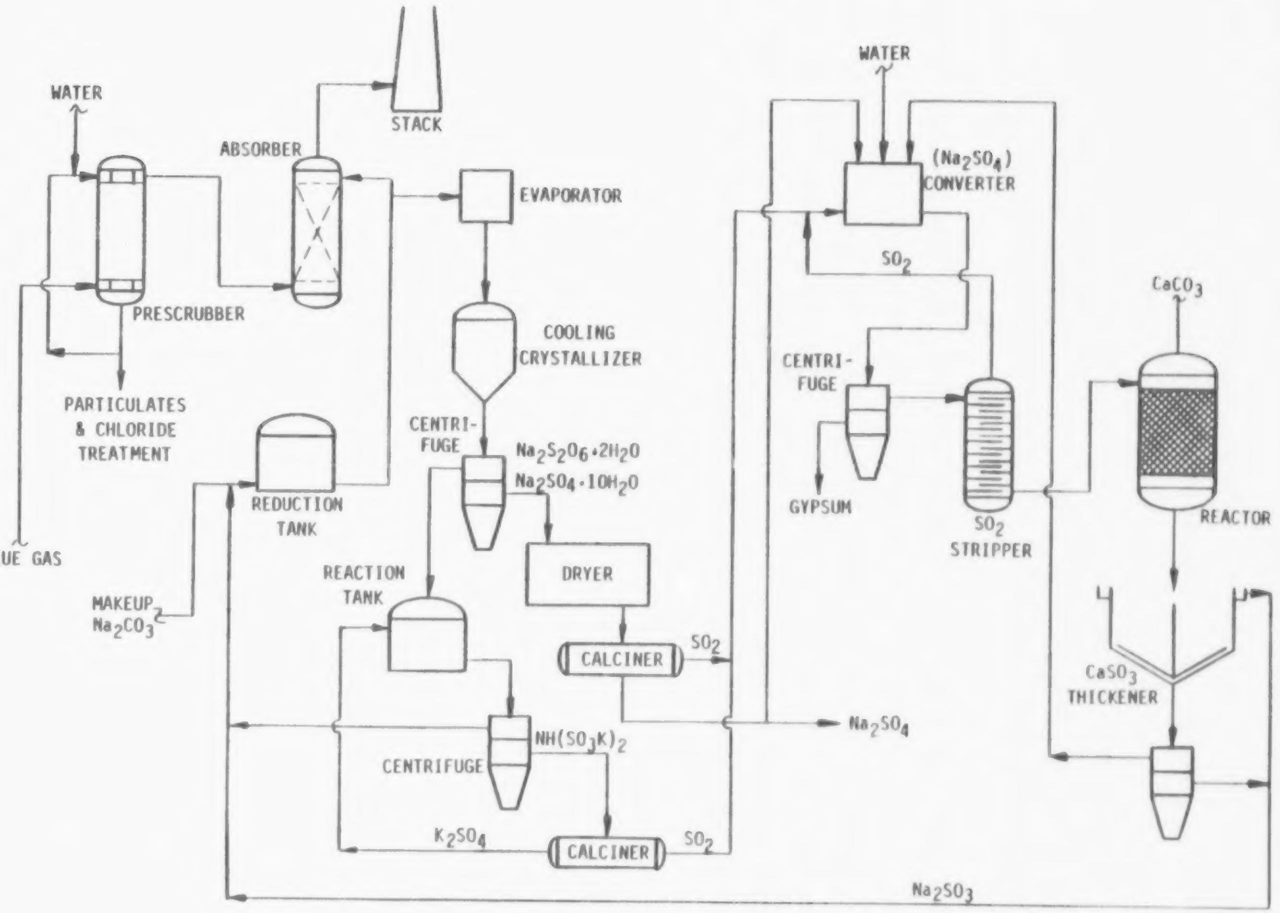
WATER
STACK
ABSORBER
EVAPORATOR
PRESCRUBBER
COOLING CRYSTALLIZER
PARTICULATES & CHLORIDE TREATMENT
REDUCTION TANK
CENTRI-FUGE
$Na_2S_2O_6 \cdot 2H_2O$
$Na_2SO_4 \cdot 10H_2O$
FLUE GAS
DRYER
MAKEUP Na_2CO_3
REACTION TANK
CALCINER
SO_2
CENTRIFUGE
$NH(SO_3K)_2$
K_2SO_4
CALCINER
SO_2
Na_2SO_3
WATER
(Na_2SO_4) CONVERTER
SO_2
CENTRI-FUGE
GYPSUM
SO_2 STRIPPER
$CaCO_3$
REACTOR
Na_2SO_4
$CaSO_3$ THICKENER

Figure 7-12. Flowsheet of the sodium process of Asahi Chemical.

and is then introduced into a scrubber. In the scrubber is it treated with a liquor at 60°C which has a pH of 6 and contains sodium sulfite, sulfate, EDTA and the ferrous ion. By using about 10 stages of perforated plates in a scrubber with a total pressure drop of 400-500 mmH_2O and L/G of 15 liter/Nm^3, about 90 percent of the NO is removed when the O_2 content of the gas is below 5 percent and the SO_2/NO mole ratio is above 3. An increase in the O_2 concentration lowers the NO_x removal efficiency slightly.

Asahi assumes the reactions to be as follows: NO forms an adduct with Fe-EDTA (equation 7-41) which reacts with sulfite and bisulfite in a "reduction tank," which is merely a holding tank to give sufficient reaction time for the formation of N_2 and sodium imidodisulfonate (equations 7-42 and 7-43). More than 99 percent of the SO_2 is also absorbed to form dithionate and bisulfite (equations 7-44 and 7-45). Those reactions also occur in the scrubber.

$$Fe^{2+} - EDTA + NO \longrightarrow Fe^{2+} - EDTA \cdot NO \qquad (7\text{-}41)$$

$$Fe^{2+} - EDTA \cdot NO + Na_2SO_3 \longrightarrow Fe^{2+} - EDTA + \tfrac{1}{2} N_2 + Na_2SO_4 \qquad (7\text{-}42)$$

$$\begin{aligned} 2Fe^{2+} - EDTA \cdot NO + 5NaHSO_3 &\longrightarrow 2NH(SO_3Na)_2 + NaHSO_4 \qquad (7\text{-}43) \\ &+ 2Fe^{2+} - EDTA + H_2O \end{aligned}$$

$$Na_2SO_3 + SO_2 + \tfrac{1}{2} O_2 \longrightarrow Na_2S_2O_6 \qquad (7\text{-}44)$$

$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \qquad (7\text{-}45)$$

$$Na_2SO_3 + \tfrac{1}{2} O_2 \longrightarrow Na_2SO_4 \qquad (7\text{-}46)$$

Most of the liquor discharged from the reduction tank is recycled to the absorber; a portion is sent to an evaporator and the concentrated liquor is then cooled to about 10°C by water and a refrigerator to crystallize sodium dithionate and sulfate. These salts are centrifuged, dried

dried and calcined at about 400°C to decompose dithionate to sulfate and SO_2 (reaction 7-47). The SO_2 and most of the sulfate are sent to a sulfate convertor. Most of the liquor discharged from the centrifuge is returned to the scrubbing system. A portion of the liquor is treated with potassium sulfate to precipitate potassium imidodisulfonate (reaction 7-48) which is much less soluble than sodium imidodisulfonate (Figure 7-13). The potassium imidodisulfonate is separated by a centrifuge and calcined at about 500°C to recover potassium sulfate and concentrated SO_2 (reaction 7-49). The sulfate is recycled and the SO_2 is sent to the sulfate convertor.

$$Na_2S_2O_6 \longrightarrow Na_2SO_4 + SO_2 \qquad (7\text{-}47)$$

$$2NH(SO_3Na) + K_2SO_4 \longrightarrow Na_2SO_4 + 2NH(SO_3K) \qquad (7\text{-}48)$$

$$2NH(SO_3K) + \tfrac{1}{2}\,O_2 \longrightarrow K_2SO_4 + SO_2 + N_2 + H_2O \qquad (7\text{-}49)$$

The sulfate conversion step and the subsequent steps are the same as those in the sodium-limestone double alkali processes developed by both Kureha-Kawasaki and Showa Denko and applied to many commercial FGD plants. The reactions in the convertor are as follows:

$$CaSO_3 + SO_2 + H_2O \longrightarrow Ca(HSO_3)_2 \qquad (7\text{-}50)$$

$$Ca(HSO_3)_2 + Na_2SO_4 + 2H_2O \longrightarrow 2NaHSO_3 + CaSO_4\cdot 2H_2O \qquad (7\text{-}51)$$

The by-product gypsum slurry is centrifuged. The mother liquor is sent to a stripper to decompose the remaining calcium bisulfite and to recover SO_2 which is sent to the sulfate convertor.

$$Ca(HSO_3)_2 \xrightarrow{\text{Heat}} CaSO_3 + SO_2 + H_2O \qquad (7\text{-}52)$$

The liquor discharged from the stripper contains sodium bisulfite with some unreacted sodium sulfate and calcium sulfite. It is treated with

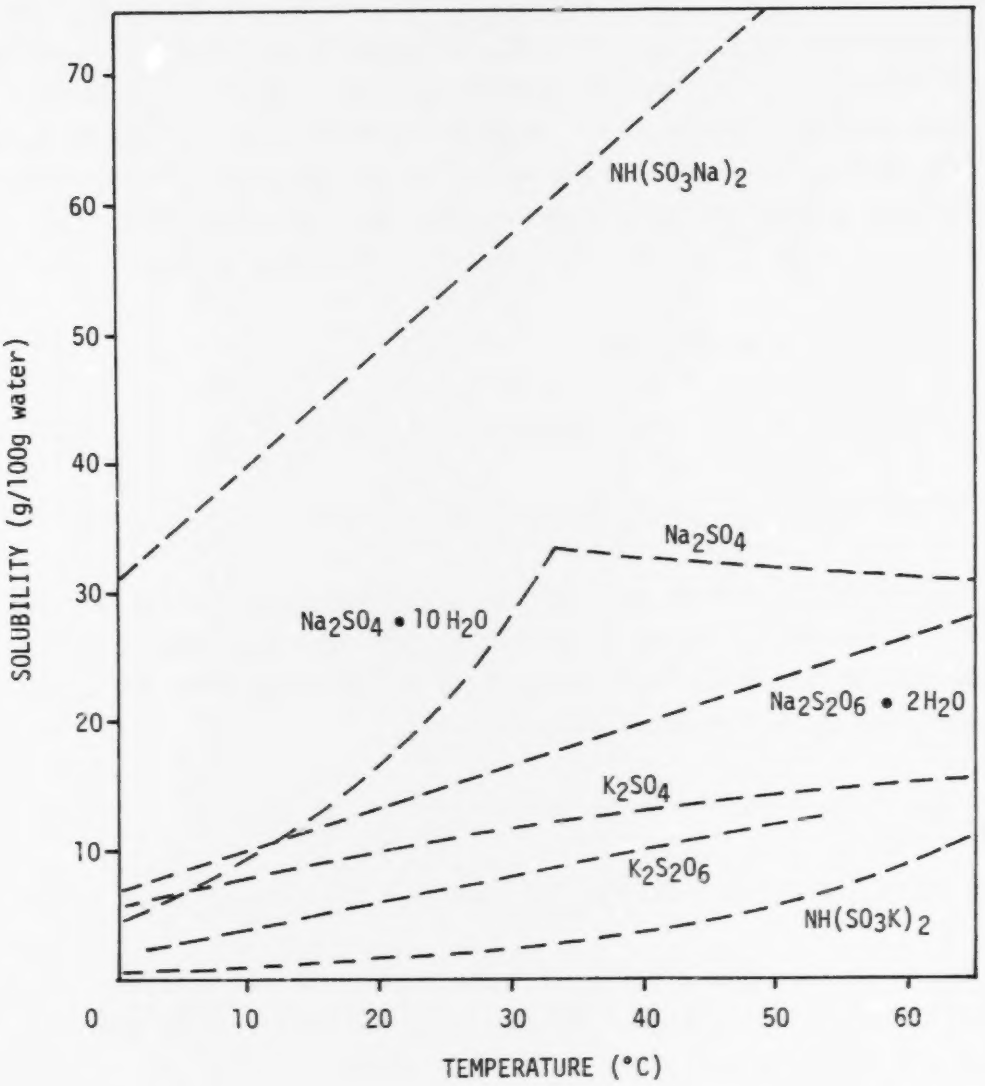

Figure 7-13. Solubilities of sodium and potassium imidodisulfonates as a function of temperature.

limestone in a reactor to recover sodium sulfite which is returned to the absorbing system. Calcium sulfite precipitated in the reactor is sent to the sulfate converter.

$$2NaHSO_3 + CaCO_3 \longrightarrow Na_2SO_3 + CaSO_3 \cdot \tfrac{1}{2} H_2O + \tfrac{1}{2} H_2O + CO_2 \qquad (7\text{-}53)$$

From the results of the tests with different gas compositions, it is estimated that when a typical flue gas from a coal-fired boiler is treated, about 93 percent of the absorbed SO_2 is converted to gypsum while about 7 percent is converted to sodium sulfate.

7.6.3 Evaluation

Although the Asahi Chemical process is not simple, it is a combination of commercially proven processes and operation of the whole system may be feasible. The vessels other than the prescrubber and the absorber are small because only the separated sodium and potassium salts are treated in them. The loss of EDTA must be very small because the salts are separated from the liquor containing EDTA and the liquor is returned to the absorbing step. Even when the thermal treatment and regeneration steps have to be shut down, the scrubber system can continue operation for a while. Operation of a larger pilot plant will be needed for a reliable cost estimation for the process.

7.7 KUREHA CHEMICAL WET SIMULTANEOUS REMOVAL PROCESSES

7.7.1 Introduction

Kureha Chemical is a medium-size chemical company credited with developing many new processes in petrochemical and electrochemical fields as well as in FGD. These processes have been licensed to many countries. Kureha modified the sodium acetate FGD process and developed a simultaneous removal process by which SO_x is converted to gypsum while NO_x is converted into NH_3. In cooperation with the Federation of Electric Companies, they operated a pilot plant which could treat 5000 Nm^3/hr of the flue gas from an oil-fired boiler.

7.7.2 By-Product Gypsum and Ammonia Process

A flowsheet of the gypsum and ammonia by-production process is shown in Figure 7-14. Flue gas containins SO_x and NO_x is treated in a packed tower with a liquor at a pH of nearly 6. The liquor contains sodium acetate, a catalyst (ferrous ion and EDTA), and a small amount of seed crystals of gypsum. The following reactions occur in the scrubber:

$$SO_2 + 2CH_3COONa + H_2O \longrightarrow Na_2SO_3 + 2CH_3COOH \tag{7-54}$$

$$2NO + 5Na_2SO_3 + 4CH_3COOH \longrightarrow 2NH(SO_3Na)_2 + 3Na_2SO_4 + 4CH_3COONa + H_2O \tag{7-55}$$

$$2NO_2 + 7Na_2SO_3 + 4CH_3COOH \longrightarrow 2NH(SO_3Na)_2 + 3Na_2SO_4 + 4CH_3COONa + H_2O \tag{7-56}$$

A small amount of acetic acid formed by reaction 7-54 is volatilized from the absorption section (packed tower) and is caught by the water scrubber at an upper part of the absorber with perforated plates. Sodium sulfite is also formed by reaction 7-54. NO_x in the gas is reacted with the sodium sulfite in the presence of catalysts to form sodium imidodisulfonate and sulfate (reactions 7-55 and 7-56).

The liquor discharged from the scrubber is treated with lime in a reactor. The following reactions occur in the reactor:

$$2CH_3COOH + Ca(OH)_2 \longrightarrow (CH_3COO)_2Ca + 2H_2O \tag{7-57}$$

$$Na_2SO_4 + (CH_3COO)_2Ca + 2H_2O \longrightarrow CaSO_4 \cdot 2H_2O + 2CH_3COONa \tag{7-58}$$

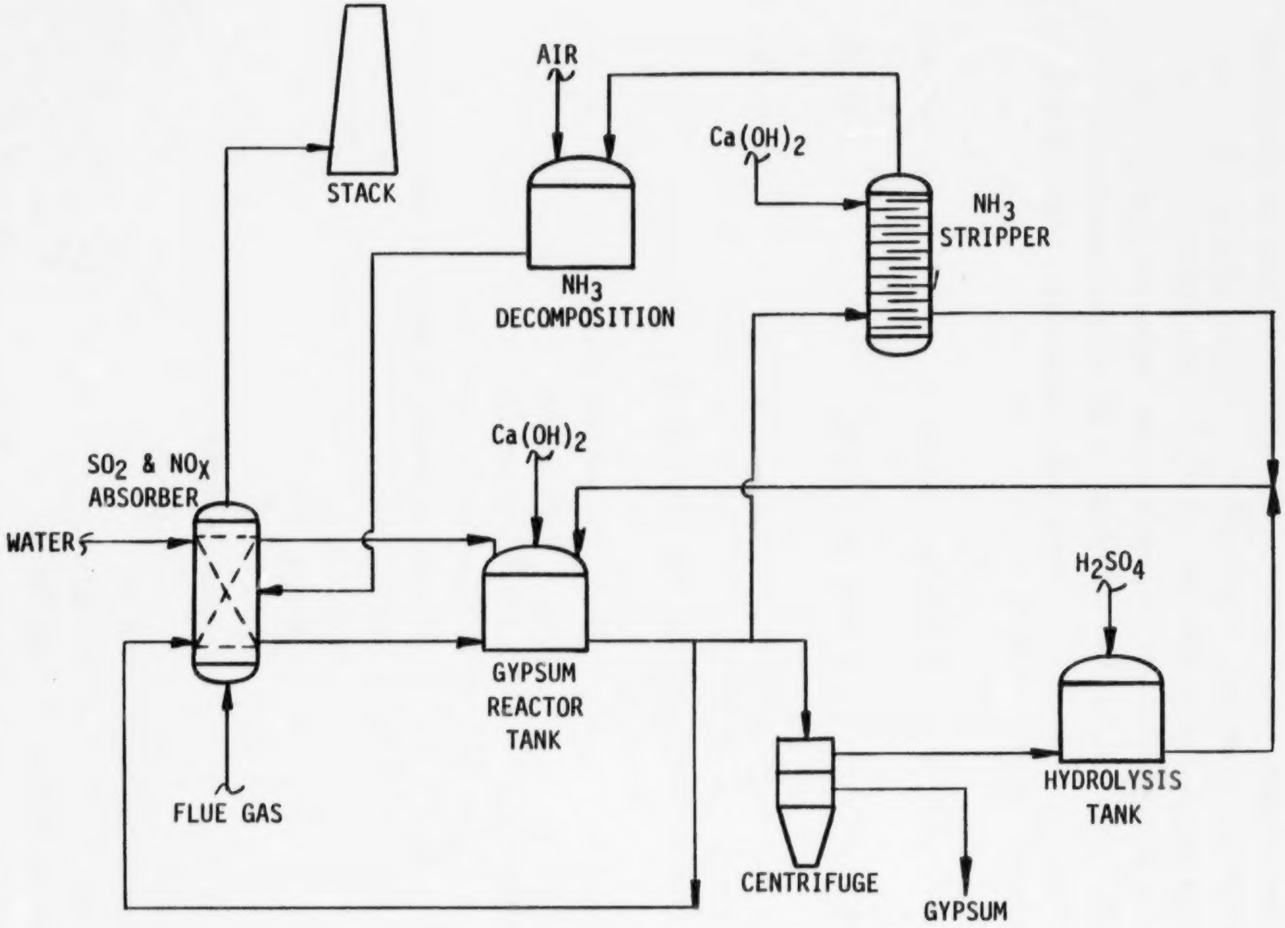
STACK
AIR
NH_3 DECOMPOSITION
$Ca(OH)_2$
NH_3 STRIPPER
SO_2 & NO_X ABSORBER
WATER
$Ca(OH)_2$
GYPSUM REACTOR TANK
H_2SO_4
FLUE GAS
HYDROLYSIS TANK
CENTRIFUGE
GYPSUM

Figure 7-14. Block flow diagram of the Kureha NDSN gypsum and ammonia by-product process for simultaneous removal of SO_2 and NO_x.

Acetic acid reacts with lime to form calcium acetate, which reacts with sodium sulfate to precipitate gypsum (reactions 7-57 and 7-58). The gypsum is centrifuged. Most of the liquor discharged from the centrifuge is returned to the absorber. A portion of the liquor is acidified with sulfuric acid and heated to 120-130°C under 2-3 atmospheric pressure to decompose the imidodisulfonate (reaction 7-59). Ammonium bisulfate formed by the decomposition is reacted with lime to precipitate gypsum and to release ammonia. The ammonia is decomposed by catalytic oxidation when no use can be found (reaction 7-61).

$$NH(SO_3Na)_2 + 2H_2O \longrightarrow NH_4HSO_4 + Na_2SO_4 \tag{7-59}$$

$$NH_4HSO_4 + Ca(OH)_2 \longrightarrow CaSO_4 \cdot 2H_2O + NH_3 \tag{7-60}$$

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \tag{7-61}$$

Operation data of the pilot plant are shown below.

NO_x (ppm):	Inlet, 200; outlet, 30-40
SO_x (ppm):	Inlet, 1500; outlet, 1
O_2 (percent):	2.1-4.2 (in and out)
L/G:	28 liters/Nm^3
Pressure Drop:	200 mmH_2O through the whole system
Raw Materials (kg/hr):	$Ca(OH)_2$, 33
	H_2SO_4, 13
	CH_3COOH, 0.2
	NaOH, 0.1
By-Product:	Gypsum, 76 kg/hr
Utilities:	
Electric Power:	205 kW
Steam:	60 kg/hr
Process Water:	250 kg/hr

A scaling problem was encountered at an early stage of operation but was solved by adding gypsum crystal seeds.

7.7.3 By-Product Sulfur and Ammonia Process

A flowsheet of the sulfur and ammonia by-product process is shown in Figure 7-15. Flue gas is first treated in a prescrubber with water to remove particulates and chlorine and then introduced into a scrubber (absorber). There it is treated with a liquor containing potassium sulfite, EDTA and the ferrous ion. More than 99 percent of the SO_2 and over 90 percent of the NO_x are removed at an L/G ratio of 10 liters/Nm^3 by the following reactions:

$$K_2SO_3 + SO_2 + H_2O \longrightarrow 2KHSO_3 \qquad (7\text{-}62)$$

$$2K_2SO_3 + 2SO_2 + O_2 \longrightarrow 2K_2S_2O_6 \qquad (7\text{-}63)$$

$$2NO + 4KHSO_3 + K_2SO_3 \longrightarrow 2NH(SO_3K)_2 + K_2SO_4 + H_2O \qquad (7\text{-}64)$$

The liquor leaving the scrubber at 55°C is evaporated under a vacuum to crystallize potassium sulfate K_2SO_4, dithionate $K_2S_2O_6$, and imidodisulfonate $NH(SO_3K)_2$. The solids are filtered and sent to a hydration and decomposition step where the following reactions occur at 280-300°C:

$$NH(SO_3K)_2 + 2H_2O \longrightarrow NH_4HSO_4 + K_2SO_4 \qquad (7\text{-}65)$$

$$K_2S_2O_6 \longrightarrow K_2SO_4 + SO_2 \qquad (7\text{-}66)$$

Most of the SO_2 formed by reaction 7-66 is sent to a Claus plant to maintain the stoichiometric ratio of H_2S and SO_2. The rest of the SO_2 is returned to the prescrubber to promote the absorption of NO_x.

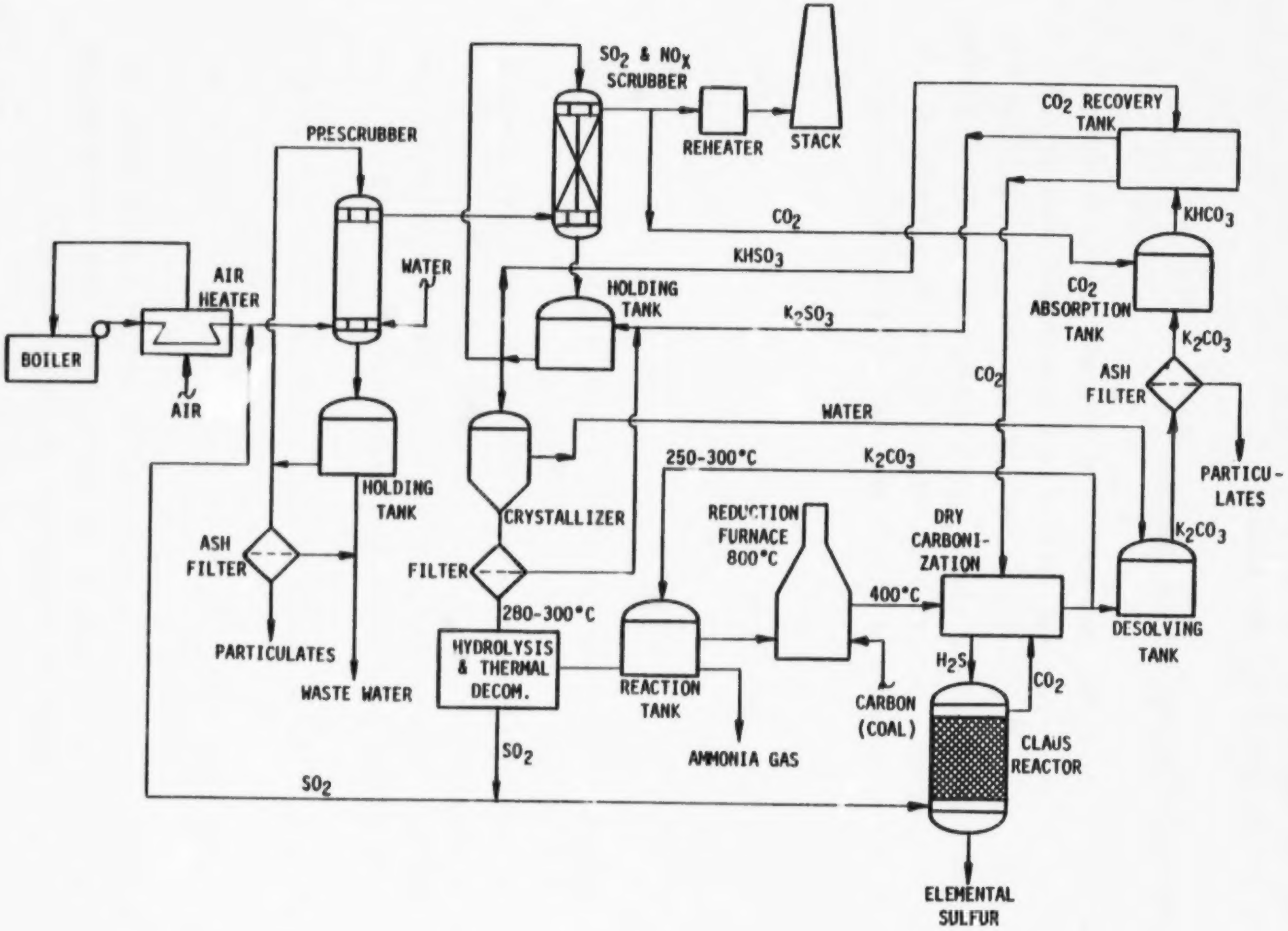
BOILER
AIR HEATER
AIR
PRESCRUBBER
WATER
HOLDING TANK
ASH FILTER
PARTICULATES
WASTE WATER
SO_2 & NO_X SCRUBBER
REHEATER
STACK
HOLDING TANK
CRYSTALLIZER
FILTER
280-300°C
HYDROLYSIS & THERMAL DECOM.
SO_2
SO_2
CO_2
$KHSO_3$
K_2SO_3
WATER
250-300°C
K_2CO_3
REACTION TANK
AMMONIA GAS
REDUCTION FURNACE 800°C
CARBON (COAL)
400°C
DRY CARBONIZATION
H_2S
CO_2
CLAUS REACTOR
ELEMENTAL SULFUR
CO_2
CO_2 RECOVERY TANK
$KHCO_3$
CO_2 ABSORPTION TANK
K_2CO_3
ASH FILTER
PARTICULATES
K_2CO_3
DESOLVING TANK

Figure 7-15. Flowsheet of the Kureha KDSN sulfur and ammonia by-production process for the simultaneous removal of SO_x and NO_x.

Ammonium bisulfate formed by reaction 7-65 is treated with potassium carbonate to release ammonia (reaction 7-67).

$$NH_4HSO_4 + K_2CO_3 = K_2SO_4 + NH_3 + H_2O + CO_2 \quad (7\text{-}67)$$

Potassium sulfate is reduced by coal at 800°C to produce potassium sulfide and carbonate (reactions 7-68 - 7-70).

$$K_2SO_4 + 2C \longrightarrow K_2S + 2CO_2 \quad (7\text{-}68)$$

$$K_2SO_4 + 4C \longrightarrow K_2S + 4CO \quad (7\text{-}69)$$

$$K_2SO_4 + 2C \longrightarrow K_2CO_3 + CO + S \quad (7\text{-}70)$$

The solids are treated with CO_2 and steam at 400°C (dry carbonization) to convert the sulfide into carbonate and to release hydrogen sulfide, which is then sent to the Claus furnace to produce elemental sulfur.

$$K_2S + CO_2 + H_2O \longrightarrow K_2CO_3 + H_2S \quad (7\text{-}71)$$

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \quad (7\text{-}72)$$

Potassium carbonate is dissolved in water (condensate from the vacuum crystallizer) and the resulting liquor is filtered to remove coal ash.

Since reaction 7-71 requires a large amount of CO_2 gas, a portion of the flue gas leaving the scrubber is treated with the potassium carbonate liquor to recover CO_2 (reaction 7-73).

$$K_2CO_3 + H_2O + CO_2 = 2KHCO_3 \quad (7\text{-}73)$$

The resulting liquor is reacted with a portion of the liquor leaving the scrubber which contains potassium bisulfite to form potassium sulfite and to release CO_2. The potassium sulfite is returned to the absorbing system; the CO_2 is used for reaction 7-71.

$$KHCO_3 + KHSO_3 \longrightarrow K_2SO_3 + CO_2 + H_2O \qquad (7\text{-}74)$$

Kureha has operated the whole system at a pilot plant which can treat 200 Nm^3/hr of flue gas. A larger scale test (3000 Nm^3/hr equivalent) was carried out for the reduction of potassium sulfate.

7.7.4 Evaluation

The gypsum and ammonia by-production process is fairly simple and can remove 99 percent of the SO_x with 90 percent of the NO_x, but it requires a large L/G ratio of about 30 and a considerable amount of sulfuric acid. The consumption of EDTA seems pretty large because the liquor containing EDTA is treated in the hydrolysis step at 120-130°C. Separation of EDTA from the liquor prior to the hydrolysis substantially lowers the consumption but complicates the system.

The sulfur and ammonia by-product process is fairly complex, but it may be the only process currently available for conversion of both SO_x and NO_x to useful by-products. It can remove over 99 percent of the SO_x with over 90 percent of the NO_x at an L/G ratio of 10. Consumption of EDTA should be very small because the potassium salts are separated from the liquor containing EDTA and all of the liquor is returned to the scrubber. Consumption of potassium may not be large; however, since coal is used to reduce potassium sulfate, some of the potassium is discarded with the fly ash that is also formed.

Although the process includes many operations for thermal treatment and recovery, the vessels for these operations are much smaller than those for scrubbing systems because only the separated potassium salts are treated in them. Moreover, even when the thermal treatment and recovery operations must be shut down, the scrubbing system can continue to operate for a considerable period.

The dry carbonization step developed by Kureha seems advantageous over the conventional wet carbonization step in which various compounds other than H_2S and K_2CO_3 are formed by side reactions.

When the ammoina by-product is not wanted, the process can be simplified because the hydrolysis and ammonia production steps are eliminated.

Further evaluation and a reliable cost estimation for both processes would require continuous operation of a larger plant.

7.8 CHIYODA THOROUGHBRED 102 PROCESS

7.8.1 Introduction

Chiyoda Chemical Engineering and Construction Co. has modified the Thoroughbred 101 FGD process to remove NO_x simultaneously. Flue gas, after being cooled in a prescrubber, is injected with ozone and is treated in a scrubber with dilute sulfuric acid containing ferric sulfate in the same way as with the 101 process. Most of the NO_x is converted to HNO_3 while a portion is converted to N_2 and a small portion to N_2O. Absorbed SO_2 is converted to H_2SO_4. The liquor is reacted with limestone to precipitate gypsum. Since the waste liquor contains calcium nitrate, it is treated with activated sludge to remove the nitrate. A pilot plant with a capacity of 1000 Nm^3/hr was operated. By using 1.5 mole O_3 for every mole of NO_x in flue gas, 90 percent of the SO_2 and 80 percent of the NO_x were removed.

7.8.2 Process Description

The process flow diagram is given in Figure 7-16. The total process consists of 6 sections: prescrubbing, ozone oxidation, absorption, SO_2 oxidation, gypsum production, and liquid waste disposal sections.

Prescrubbing--

Flue gas from a boiler is first scrubbed with water to be cooled approximately to its adiabatic saturation temperature. A large portion of the particulates in the gas and some of the sulfur trioxide are removed in the prescrubber.

Ozone Oxidation--

Ozone is then injected into the gas to oxidize the NO to NO_2 and N_2O_5. SO_2 is not oxidized by ozone. The main reactions in this section are as follows:

$$NO + O_3 \xrightarrow{\text{Fast}} NO_2 + O_2 \qquad (7\text{-}75)$$

$$2NO_2 + O_3 \xrightarrow{\text{Slow}} N_2O_5 + O_2 \qquad (7\text{-}76)$$

Absorption--

At the absorption stage, the gas is scrubbed to remove SO_2, NO_2, N_2O_5 and O_3 by an absorbent. The absorbent is a solution of dilute sulfuric and nitric acids and ferric ions as catalyst; it is saturated with dissolved oxygen. SO_2, NO_2, N_2O_5, and O_3 are absorbed into the liquid phase.

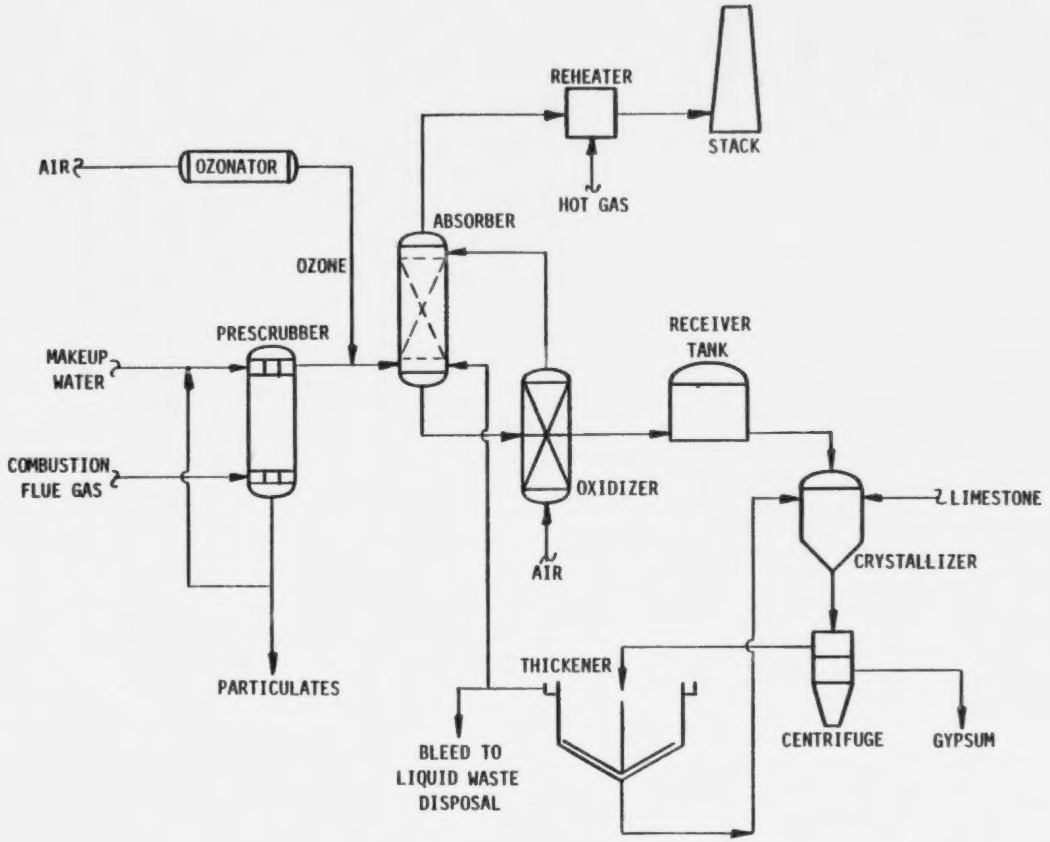
AIR
OZONATOR
OZONE
REHEATER
STACK
HOT GAS
ABSORBER
PRESCRUBBER
MAKEUP WATER
COMBUSTION FLUE GAS
RECEIVER TANK
OXIDIZER
LIMESTONE
CRYSTALLIZER
AIR
PARTICULATES
THICKENER
BLEED TO LIQUID WASTE DISPOSAL
CENTRIFUGE
GYPSUM

Figure 7-16. Schematic process flow diagram of the Chiyoda Thoroughbred 102 process.

The reactions in the absorber are as follows:

$$SO_2 + H_2O \longrightarrow H_2SO_3 \quad (7\text{-}77)$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \quad (7\text{-}78)$$

$$N_2O_5 + H_2O \longrightarrow 2HNO_3 \quad (7\text{-}79)$$

$$2H_2SO_3 + O_2 \xrightarrow{Fe^{3+}} 2H_2SO_4 \quad (7\text{-}80)$$

$$2HNO_2 + 2H_2SO_3 \longrightarrow N_2O + 2H_2SO_4 + H_2O \quad (7\text{-}81)$$

$$2HNO_2 + 3H_2SO_3 \longrightarrow N_2 + 3H_2SO_4 + H_2O \quad (7\text{-}82)$$

SO_2 Oxidation--

The absorber effluent liquid is pumped into a bubble column oxidizer, where H_2SO_3 is oxidized into sulfuric acid by air injected at the bottom of the oxidizer.

The liquid, saturated with oxygen, is circulated back to the absorber.

Gypsum Production--

A portion of the absorbent is transferred to the crystallizer and charged with limestone slurry to precipitate gypsum crystals. The by-product gypsum crystals are continuously separated from the liquid by a centrifuge. The mother liquor is returned to the absorption section.

Liquid Waste Disposal--

A small amount of mother liquor is continuously bled from the liquid return stream to maintain a constant nitric acid concentration level and also to limit the accumulation of heavy metals and other undesirable salts which come into the system from the flue gas, makeup water, and limestone. The catalyst (ferric ion) is recovered by precipitation in the form of $Fe(OH)_3$ by neutralization and reused. Nitrate ion, thereafter, can be removed by biological treatment under anaerobic conditions. Nitrate is reduced to nitrogen gas by adding methanol while the liquor is neutralized by sulfuric acid injection. Reduction is performed in two stages. Methanol is used in excess and removed biologically under aerobic conditions before final purge.

7.8.3 Economics

Only ozone generators need be added to the Thoroughbred 101 plant for the Thoroughbred 102 process. Almost all of the cost for NO_x removal is that for generating ozone. Overall power consumption for ozone generation is 23-26 kWh/kg-O_3. The cost for ozone is 500-700 yen/kg-O_3 ($2.50-3.50/kg-$O_3$) for ozone generators with a 100-500 kg/h capacity at 70-90 percent operation.

Table 7-6 shows the capital investment cost for the Thoroughbred 102 process and the removal costs for NO_x and SO_2. The costs include those for waste liquor treatment.

Requirements for the wastewater treatment system are shown in Table 7-7. When flue gas at 650,000 Nm^3/hr is treated to reduce NO_x from 120 to 30 ppm (75 percent removal), the amount of wastewater is 10 m^3/hr. The 3300 ppm of NO_3^- in the water is reduced to 30 ppm, which is about equal to the concentration after city sewage water is treated by an activated sludge process.

The operation cost including 25 percent of the investment cost at 6000 hours' yearly operation is 17,000 yen/hr ($85/hr) or 1700 yen/$m^3$ ($8.50/$m^3$) of water and is equivalent to 360 yen/kl ($1.80/kl) oil.

TABLE 7-6. CAPITAL INVESTMENTS AND OPERATING COSTS FOR THE THOROUGHBRED 102 PROCESS

Basis of Calculation:

NO Concentration = 150 ppmv at 8 vol. percent moisture
SO_2 Concentration = 1000 ppmv
NO_x Removal Ratio = 80 percent
SO_2 Removal Ratio = 90 percent
Annual Operating Ratio = 90 percent

Flue Gas Capacity (Nm^3/h)	Plant Sections	Capital Cost (10^6 yen, \$5000)	Operating Cost* (yen/kl fuel, \$0.005/kl)
300,000	Ozone Generator	1300	3600
	Absorber and Other Equipment	2500	5600
450,000	Ozone Generator	1900	3500
	Absorber and Other Equipment	3500	5400
750,000	Ozone Generator	3000	3400
	Absorber and Other Equipment	5000	5000

* Operating cost includes fixed cost, actual operating cost as well as depreciation allowance.

TABLE 7-7. REQUIREMENTS FOR WASTEWATER TREATMENT (CHIYODA 102 PROCESS)

Plant Cost:	180 million yen (\$900,000)
Site Requirement	30 m x 18 m
Requirements for Operation:	
Electric Power	80 kW
Methanol	73 kg/hr
H_2SO_4	115 kg/hr
H_3PO_4	2.4 kg/hr
$FeCl_3$	0.9 kg/hr
Labor	0.5 man per shift

7.8.4 Evaluation

The Thoroughbred 102 process is simple and can remove about 80 percent of the NO_x simultaneously with over 90 percent of the SO_2. The catalyst is neither expensive nor hazardous to the environment. Although waste liquor treatment is needed to remove the nitrate, the treatment does not cost much.

The major disadvantage of the process is the requirement of a large amount of ozone--1.5 moles for each mole of NO. The process should be used for flue gas from a boiler with extensive combustion modification to reduce NO_x.

7.9 OTHER WET PROCESSES

7.9.1 Permanganate Processes

Nissan Engineering, a subsidiary of Nissan Chemical, developed a sodium permanganate process and constructed 4 small commercial plants to treat 100-2000 Nm^3/hr of the flue gases from plants using nitric acid. Mitsubishi Metal, jointly with Mitsubishi Kakoki Kaisha and Nippon Chemical, developed a potassium permanganate process and operated a pilot plant capable of treating 4000 Nm^3/hr of flue gas.

In both processes, NO_x is absorbed by a permanganate solution to form nitrate or nitrite, while the permanganate is converted to manganate or manganese dioxide. The manganate or manganese dioxide is converted to permanganate by chemical processes including electrolytic oxidation.

Although over 90 percent NO_x can be removed, the regeneration of the permanganate is costly. Treatment of the by-product liquor containing the nitrate or nitrite is not easy. Moreover, when the gas contains SO_2, the permanganate is consumed by the SO_2. Therefore, use of the process may be limited to a small amount of gas containing no SO_2.

7.9.2 Equimolecular Absorption

Kawasaki Heavy Industries tested magnesium scrubbing of flue gas (5000 Nm^3/hr) from a coal-fired boiler. NO_2, equimolecular to NO in flue gas, is added to the gas and the gas is subjected to magnesium scrubbing to form magnesium nitrite and sulfite. The liquor is oxidized by air and treated with sulfuric acid to generate NO_x in an amount equal to that of inlet NO. The NO_x is air-oxidized to NO_2 and injected into flue gas. The resulting liquor is treated with lime to precipitate gypsum. Calcium nitrate is also obtained as a by-product. The process was abandoned because of the low NO_x removal efficiency and the difficulty in disposing of the calcium nitrate.

7.9.3 Others

The processes by Shirogane and Osaka Soda (Table 7-1) are similar to the sodium process by Sumitomi-Fujikasui (Section 7.4.1) except that Shirogane uses ozone as the oxidizing agent. The Shirogane process may not be suitable for large plants because of the consumption of the oxidizing agent and sodium hydroxide and the problem of the wastewater treatment.

Kobe Steel, Hodogaya, and Mitsui Engineering have given up the operation of the pilot plants shown in Table 7-1 or have been trying to change the process.

7.10 REFERENCES

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